Mississippi Pultrusion

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

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Recent Publications

Ellen Lackey, Kapil Inamdar, Leah Worrel, Walid Al-Akhdar, and D. A. Wostratzky, "Demonstration and Development of Filament Winding using Photoinitiated Resins," *RadTech Report*, May/June, pp. 36 – 42, 2001.
Brief Abstract: Photoinitiated resins offer an alternative to resin systems utilizing peroxide catalysts that are typically used with the filament winding process. Results from the filament winding experiments demonstrate that photoinitiated resins are viable materials for use with composites processing. A desired combination of through cure and surface cure was achieved when a combination of BAPO and AHK was used.

Ellen Lackey, James G. Vaughan, and Michael Frazier, "Experimental Examination of the Use of Self-Tapping Screw for Mechanical Attachments," *Revolutionary Materials: Technology and Economics – International SAMPE Technical Conference Series*, Vol. 32, pp. 484 – 497, 2000.
Brief Abstract: The major focus of the study was the use of self-tapping screws for mechanical attachments to SCRIMP'ed FRP sandwich panels with a balsa core. Evaluation of the self-tapping screw attachments was conducted under static uniaxial loading, static shear loading, and combined shear and axial static loading. Discussion of both failure loads and failure mechanisms seen for the self-tapping screw attachments is presented.

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CMRG Researchers Team with J. M. Huber Engineered Materials Division Researchers to Understand the Effects of Kaolin Clay Fillers in Pultrusion

Researchers at the Composite Materials Research Group (CMRG) at the University of Mississippi (UM) have recently been involved in a research study designed to improve the understanding of the effects that inorganic fillers have in pultrusion. This research is being conducted with researchers from the Engineer Materials Division of J. M. Huber. Preliminary work previously performed by UM demonstrated that filler materials have a significant effect on mechanical properties such as fatigue life; however, a more complete understanding of which specific variables associated with the filler affect the properties of the pultruded composites must be developed. The goal of this research project is to increase the understanding of how and why filler characteristics affect properties and processing of pultruded composites. The initial phase of the research has focused on kaolin clays.

Kaolin clay is defined as a rock mass that is composed essentially of the clay mineral kaolinite whose particles are comprised of primary crystals that occur in the form of pseudo-hexagonal platelets. In the selection of a mineral filler for composite processing, two main characteristics to be considered are cost and performance. Differences in physical and chemical properties among different kaolin clays may affect the performance characteristics of the materials.

In this research project, CMRG researchers have conducted pultrusion experiments to evaluate the effects of various kaolin clays in the pultrusion process. Complementing these ef-

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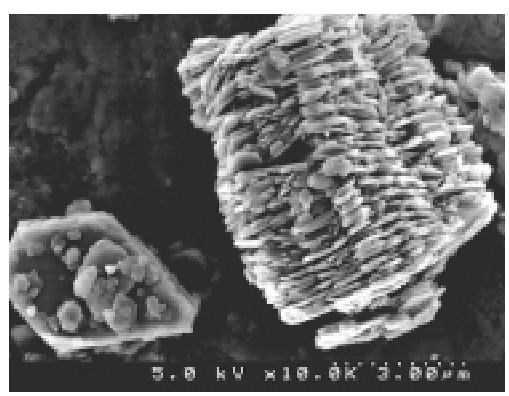

Example of the morphology of a kaolin clay.

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 kinetic modeling, and experimental characterization/optimization. In this issue of *Mississippi Pultrusion*, a discussion of continuing research concerning the effect of fillers on the properties of pultruded composites is presented.

Understanding the Effect of Kaolin Clays in Pultrusion

Kaolin clays are often utilized as resin filler materials in the fabrication of pultruded composites. While many members of the pultrusion community consider resin fillers simply to be inexpensive, space-filling materials, inorganic fillers are actually an integral part of the overall composite material. Just as careful consideration is given to the selection of appropriate fiber reinforcement and matrix material for a given application, similar consideration should be given to the selection of appropriate filler materials. The addition of inorganic fillers to the pultrusion resin system can facilitate the fabrication of the composite and can influence the properties of these materials. As a follow-up to previous research that demonstrated the significant influences that fillers can have on the properties of pultruded composites, this study is intended to begin to develop a more complete understanding of which specific variables associated with the mineral fillers affect the properties of the pultruded composites.

Minerals Examined: This study utilized various commercially available and specially prepared kaolin clay materials for pultrusion processing. The kaolin clays examined were produced with different mineral processing techniques; different median particle size, particle size distribution, particle geometry; and different chemical surface treatments. A brief description of each kaolin clay evaluated in this study is given in Table 1.

Property Evaluation: Mechanical and physical property testing of the minerals, mixed resin, and pultruded composites was conducted to characterize the materials and evaluate the effects of the kaolin fillers on the resultant properties and processing of the composites.

The median and mean particle size values of the test clays, as measured in water with a Cilas Model 920L laser light-scattering (LLS) particle size analyzer, are summarized in Table 2. The particle size values, reported in microns, were determined two different ways: 1) cell disrupted which employs the use of ultrasonics to aid in the aqueous dispersion and break-up of any clay particle agglomerates; and 2) non-cell disrupted wherein ultrasonics are not employed. The differences seen in particle size values obtained by these two methods are indicative of the ultimate primary particle size of the clay versus its original agglomerate size before dispersion. The BET surface area properties of the clays were determined using a Micromeritics Gemini 2360 unit by the nitrogen absorption method. Multi-point and Single Point BET data were collected and are reported in Table 2. Scanning electron microscopy (SEM) was used to obtain micrographs of the kaolin clays. The clay particle size distribution curves were all determined with a Malvern Mastersizer E laser light-scattering particle size analyzer using aqueous dispersions of the test clays which had been prepared with high-shear mixing conditions in combination with a low molecular weight sodium polyacrylate dispersant. The clay particle aspect ratio values were determined from Sphericity Model based calculations using experimentally determined surface area data. The viscosity of the mixed resin was recorded from the end of final resin mixing through the end of the pul-

Table 1. Kaolin clay fillers examined

Mineral Designation	Description
A (Experimental Clay DP-8064)	An ultrafine particle size, low aspect ratio kaolin clay consisting principally of individual clay platelets that is provided in a finely milled powder form.
B (Polyfil® 70)	A fine particle size, calcined kaolin clay having a randomly structured, aggregate particle morphology that is provided in a powder form.
C (Polyfil® 35)	A coarse particle size kaolin clay having a broad particle size distribution consisting principally of large booklets of clay platelets that is provided in a milled powder form.
D (Polyfil® 8039)	A coarse particle size kaolin clay having a somewhat narrower particle size distribution versus Mineral C consisting principally of large booklets of clay platelets that is provided in a milled powder form.
E (Experimental Clay DP-8065)	An intermediate particle size, delaminated kaolin clay consisting principally of individual clay platelets having a high particle aspect ratio that is provided in a milled powder form.
F (Polyfil® X)	A fine particle size, intermediate aspect ratio kaolin clay consisting principally of individual clay platelets that is provided in a finely milled powder form.
G (ASP®- 400P)	A competitive coarse particle kaolin clay similar to Mineral C.
H	Organically surface treated version of Mineral D.
I	Organically surface treated version of Mineral E.

ASP® is a product of Engelhard Corp.　　Polyfil® is a product of J. M. Huber Corp.

Table 2. Clay Properties

	Cell disrupted		Non-Cell Disrupted	BET Multi-Point	BET Single Point
	Median PS	Mean PS	Median PS	Surface Area	Surface Area
	Cilas (μm)	Cilas (μm)	Cilas (μm)	m^2/g	m^2/g
Mineral A	0.75	2.52	64.86	24.94	24.46
Mineral B	2.64	4.13	2.69	9.03	8.75
Mineral C	6.90	8.77	7.66	11.36	11.15
Mineral D	8.12	9.71	8.09	9.72	9.53
Mineral E	4.98	6.33	5.74	13.88	13.61
Mineral F	3.02	4.14	3.84	18.42	18.10
Mineral G	7.63	9.86	7.70	8.51	8.34

trusion experiment, and pull force data was recorded during the pultrusion experiments to characterize the ease of processing of each resin system. A Hegman grind gage and a stereo optical microscope were used to examine the particle size of the clays in the mixed resin. The Hegman "fineness of grind" properties of the clay filled resin systems, which can be correlated to an average filler particle size via the resultant gage readings, were determined using an adaptation of the ASTM testing procedure D 1210-96. Energy dispersive spectroscopy (EDS) was used to identify the particles seen in the samples of mixed resin. Static 3-point flexural testing, short-beam shear testing, and flexural fatigue testing were conducted to characterize the mechanical properties of the pultruded composites.

Pultruded Composite Static Mechanical Properties: Static short-beam shear testing results for the pultruded composites do not reveal significant differences in the short-beam shear strength of the pultruded composites produced with the kaolin clays. The exception to the observation that clays have little effect on static flexural properties is the composite material produced using Mineral B, the calcined kaolin clay. Both the static flexural strength and strain-to-failure for the pultruded composites with mat/unidirectional reinforcement and with unidirectional reinforcement that were formulated using Mineral B were lower than any of the other samples produced. When Mineral B was utilized for the composites with only unidirectional reinforcement, significant fuzzing and tearing of the resin-coated glass fiber was seen; this phenomena was observed for numerous replications of this experiment. It is suspected that the damage to the reinforcement that occurred when Mineral B was utilized is related to the lower flexural property data seen for these composites since flexural properties are fiber-dominated properties. If fiber damage resulting from the use of Mineral B is a reason for the observed flexural property degradation, the use of Mineral B would not be expected to significantly affect shear strength, a resin dominated property. This was the case for Material B composites, as no significant effect on shear property data was seen for the Material B samples. The lower flexural property data recorded for Material B agrees with data for another calcined clay previously observed in an earlier study. Based on these results from two different calcined kaolin clays in two different resin systems, it is apparent that the use of calcined clays should be avoided for pultruded composites. The lower flexural strength associated with the use of calcined kaolin clays is apparently a consequence of its hard and abrasive structure that tears the glass reinforcement combined with its randomly structured, aggregate morphology which lowers its effective particle aspect ratio.

Pultruded Composite Fatigue Properties: There is significant variation in fatigue lifetime dependent on the type of mineral filler used. The range of lifetime from 17,00 cycles to over 300,000 is considerable. The two longest fatigue lifetimes are associated with two of the smaller median particle size minerals (E and F); however, the clay of finest particle size, Mineral A, did not show as long of a fatigue life. This is likely a consequence of the very high resin viscosity generated by the use of Mineral A, which in turn inhibited its dispersion into the resin. Also, it was observed that the very large apparent particles associated with Mineral I produced an intermediate fatigue life that was considerably reduced in duration versus that provided by its untreated analog, mineral E. Mineral I was organically surface treated, and this treatment is the most likely cause for the decreased fatigue life. The particular surface treatment applied in this case appears to have inhibited wet-out and dispersion of the clay particles rather than helping it since its resultant particle size in the resin mix, as determined from Hegman Grind gage techniques, is larger. Correcting this dispersion problem may be a simple matter of adjusting the chemistry and polarity of the organic surface treatment and offers an interesting area for further scientific investigation. Also of interest to compare are the physical properties of Minerals E and F, which were the best performers and yielded virtually equivalent fatigue life performance. Mineral F is finer in median particle size, has a very pronounced bimodal particle size distribution, and has a significantly smaller particle aspect ratio value versus the delaminated clay, Mineral E. Thus, as seen in our previous studies, the fatigue lifetime of these clay mineral fillers does not directly correlate with their ultimate primary particle size properties (as determined from aqueous dispersion measurements) even though there is apparently some relationship. Further exploration of their performance characteristics versus actual "in use" resin particle size properties needs to be conducted.

Additional details concerning these studies are available in the *ICE '99 Proceedings of the Society of the Plastics Industry*, the *Composites '00 Proceedings of the Composite Fabricators Association*, and the *Composites '01 Proceedings of the Composite Fabricators Association.*

Recent Publications (cont.)

Gadam, J. A. Roux, T. A. McCarty and J. G. Vaughan, APressure Rise Inside a Cylindrical Pultrusion Die for Graphite/Epoxy Composites,@ *Polymers and Polymer Composites*, 8 (4) 231-244, 2000.
Brief Abstract: A three-dimensional, axisymmetric model based on Darcy's law for resin flow through a porous fiber bed in cylindrical coordinates, which employs the finite volume solution method, was developed to predict the pressure rise in a pultrusion die for graphite/epoxy composites. A variable viscosity was employed, and an anisotropic permeability model was used for calculating the permeability values in the axial and radial directions. Various process control parameters including preform plate cavity to die cavity area ratio (compaction ratio), resin viscosity, pull speed, die heating profile, and fiber volume fraction were varied to investigate their impact on the die inlet pressure rise in the pultrusion manufacturing of graphite/epoxy composites.

Ellen Lackey, et al, "Experimental Examination of Filament Winding with BAPO Photoinitiated Resins," *Technical Papers B CFA Composites 2000*, CDROM, 2000. (Selected as Best Processing Paper for Composites '00)
Brief Abstract: In this study, a variety of photoinitiators were screened for use, and the use of photoinitiated resins with the filament winding process and the fabrication of chopped glass laminates was demonstrated. Based on the results of this screening, it was determined that a combination of bisacylphosphine oxide (BAPO) and alpha hydroxy ketone (AHK) in a 1:3 ratio provided an excellent photoinitiator package that provided both surface and deep through cure.

Kaolin Clay Fillers (cont.)

forts, the researchers from J. M. Huber have characterized commercially available kaolin clays and specially prepared experimental clays. Data from these experiments have been evaluated to identify any correlation that exists between physical or chemical properties of kaolin clays and resulting effects on processing and final mechanical properties of pultruded composites.

Results from the present study support the conclusions shown in previous studies that 3-point flexural bend tests and short-beam shear static mechanical properties are not greatly affected by mineral type with the exception of the calcined clay. This study showed that calcined clays are detrimental to pultruded product mechanical properties because of the high hardness and abrasiveness of the calcined clay that appears to tear and fuzz the glass fiber combined with its randomly structured, aggregate morphology which lowers its effective particle aspect ratio.

The study identified complex interactions among particle size distribution, surface area, and particle aspect ratio of the mineral that affect fatigue life. As individual parameters, the performance data suggest that smaller particle size distribution, higher surface area, and higher particle aspect ratio are, in general, best for highest fatigue lifetime, but these three physical parameters interact with one another in a complex manner to affect fatigue lifetimes. Additional studies are being conducted to resolve these mineral property driven performance relationships.

The CMRG is committed to the development and dissemination of research data concerning the constituent materials available to pultruders. Research and development efforts such as this study offer the opportunity for the pultrusion industry to continue to expand its markets and improve the overall quality of pultruded composites.

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