Effects of Low Temperature Thermal Cycling and Moisture on Izod Notch Toughness of a Glass FRP

K. G. Kellogg and A. R. Kallmeyer
North Dakota State University, Fargo, ND, USA

P. K. Dutta
U.S. Army Cold Regions Research and Engineering Laboratory
Hanover, NH, USA

ABSTRACT

Notched Izod impact tests were conducted on wet and dry specimens of a pultruded, glass fiber-reinforced polymer composite after thermal cycling between 25 and –50ºC. Specimens were impacted following the application of 50, 150, and 300 thermal cycles. The results indicate that moisture initially had a beneficial effect on the notch toughness, probably due to a reduction in residual stresses from matrix swelling. After 300 thermal cycles, the beneficial effect of moisture was negated, likely due to an increase in damage from freeze/thaw expansion of the water, and a reduction in the overall moisture state in the composite. Further research is needed to quantify the damage accumulation during low-temperature thermal cycling.

KEY WORDS: polymer composite, notch toughness, impact, moisture, low temperatures, thermal cycling

INTRODUCTION

In the construction industry, time and money have always been two of the key issues. The race to develop products, methodologies, and/or materials that will cost less, last longer, and minimize the amount of time needed to complete a task has never been as intense as it is today. In the past 10 years, polymeric composite materials have generated considerable interest in the construction industry for some of these very reasons.

It has long been known that composite materials possess unique and beneficial properties. They have high strength-to-weight ratios, are extremely stiff, are non-magnetic and non-conductive, provide good chemical resistance, and are lightweight. In the past, the biggest drawback to the use of composite materials was the cost. However, with recent advances in materials and manufacturing techniques, cost is quickly becoming a non-issue. Manufacturers are currently producing glass-reinforced composites in structural shapes that are intended to compete one-on-one with steel and wood. Graphite fiber reinforced polymers, once attainable only by the military and aerospace industries, are now being used economically to rehabilitate deteriorating infrastructure. With the increased use of composite materials in so many arenas, it becomes imperative that engineers and scientists understand the mechanical behavior of these various material systems under all service environments.

One critical service environment for composite material usage is in cold regions. The northern latitudes of the United States can see temperatures as low as –45°C. In addition to these low temperatures, the material system may be exposed to snow, ice, or moisture. Any material system that is to be used in such an environment must be capable of handling various combinations of loading (static and cyclic), thermal cycling, moisture, ice, and snow. Unfortunately, only a small amount of information is available on the performance and material characterization of polymeric composites subjected to these environments.

In March of 1998 an NSF funded workshop was conducted at the U.S. Army Cold Regions Research and Engineering Laboratory, to "identify the research needs and establish priorities over the complete spectrum of topics pertinent to the applications of composite materials in cold regions." The Cold Regions Composites Workshop, or CRCW, offered several recommendations regarding composites and cold regions, with the overall conclusion that more research to understand the behavior of composites in cold regions is needed.

The objective of this study is to determine the effects of moisture and low-temperature thermal cycling on the parallel-to-the-fiber Izod notch toughness of a commercially available, glass fiber reinforced plastic (FRP). This information provides an assessment of the fracture toughness of the material along the fiber direction.

PREVIOUS WORK

The effect of the environment on the durability and performance of polymeric composites has long been an area of concern. The high sensitivity of polymers to moisture and elevated temperatures, coupled with the fact that numerous applications require operation in such environments, have resulted in a significant amount of research devoted to understanding and characterizing the behavior of polymer composites at elevated temperatures and moisture levels. Unfortunately, relatively few studies have been undertaken to examine the effects of reduced temperatures on the performance of these materials. As the use of polymer composites increases in both civil and military applications, cold temperature environments will be encountered more frequently, requiring a thorough understanding of the behavior and durability of composites in these environments.

An area of particular concern, with regard to environmental influences, is the ability of a composite to absorb energy during an impact event. It is well known that the impact strength and toughness of materials is strongly influenced by temperature. For most engineering materials, a reduction in temperature leads to a reduction in impact strength. However, the limited data on low temperature impact properties of polymer composites indicate that this is not always the case. For example, Voelker (1991), in a study of the notched Izod impact strength of thermoplastic composites, found that the effect of low temperatures on impact behavior depends on the material system. Considering a temperature range of 22º to −31.7ºC, long glass fiber-reinforced nylon composites showed a decrease in impact strength with decreasing temperatures, while similar composites with other polymer resins showed increases in impact strength under the same conditions. However, all short glass fiber composites considered in the study exhibited a decrease in impact strength with decreasing temperatures.

In a similar study, Dutta et al (1994a) found that the absorbed energy during Charpy impact testing of a wood fiber reinforced plastic decreased with decreasing temperature (from 50º to −60ºC), although the greatest drop was found to be between 50º and 24ºC. In contrast, Nishijima and Okada (1982) reported mixed results in the Charpy impact strength of cloth reinforced (glass and carbon fiber) epoxide resin at room temperature and liquid nitrogen temperature. They found that temperature had a varying effect on the impact strength, depending on the fiber orientation during impact. Wigley (1971), however, reported almost no change in notched impact energy from 22º to −196ºC for a high modulus carbon/epoxy laminate.

Several additional studies have focused on the influence of moisture content and low temperature on the unnotched impact strength and energy absorbing abilities during fracture of polymeric composites. Karbhari and Pope (1994) impacted glass mat reinforced, epoxy resin composites using a Dynatup drop-weight impactor. Specimens had been subjected to a variety of environmental conditions, such as water immersion, freezing in water, and low temperature conditioning. The effects of these environmental conditions on the post-impact flexure strength were evaluated, and competing effects were found. In separate studies, Dutta et al (1993, 1994b) measured the energy absorbed during impact in composites using a split Hopkinson pressure bar apparatus. Again, the results were mixed and depended on a number of factors, including temperature, moisture content, thermal cycling, and impactor velocity. In a study of mixed-mode delamination fracture in graphite/epoxy composites, Russell and Street (1985) measured an increase in fracture energy with decreasing temperature (from 100º to −50ºC). They argued that residual stresses and constraint effects may play a dominant role in the influence of temperature on delamination behavior.

As is evident, there appears to be few definable trends regarding the influence of low temperatures and moisture on the impact strength of polymer composites. In a previous study, Kellogg et al (1999) investigated the effects of moisture and reduced temperature on the notch toughness of a pultruded glass-reinforced polymer composite. Specimens were impacted with an Izod tester such that the fracture surface was parallel to the fibers. Two moisture levels were considered: dry (as received) and wet (soaked in water for 18 hours resulting in 0.018% by weight moisture content). Specimens were impacted at four temperatures, 25º, −5º, −25º, and −50ºC. The results, shown in Table 1 and Figure 1, indicate that both temperature and moisture had only a modest influence on the notch toughness of the composite. At room temperature, the mean notch toughness of the wet samples was approximately 15% higher than that of the dry specimens. A possible explanation for this behavior is that swelling of the matrix due to moisture absorption may relieve some of the residual stresses in the matrix that are caused by cool-down from curing temperatures. However, at temperatures of −5º and −25ºC, there is very little difference in mean toughness values between the wet and dry specimens, indicating that the beneficial effects of moisture are negated when the moisture freezes. At −50ºC, both sets of specimens showed a noticeable increase in notch toughness values. It is believed that the increased strength and stiffness of the polymer resin at very low temperatures becomes more influential on impact energy values than does the presence of moisture within the composite. Another important trend that can be seen from the data in Figure 1 is the increase in scatter in the wet samples. Clearly, the introduction of moisture into the material resulted in greater scatter in impact energy values at all temperatures. This result is important to engineers who must consider the lower bounds in specifying design allowables.

The objective of the present study was to further investigate the influence of moisture and reduced temperatures on the notch toughness of this pultruded composite. Specifically, the effect of thermally cycling the material between 25º and −50ºC was studied, to determine whether repeated freezing and thawing of moisture within the material would degrade the structural properties of the composite, due to the expansion and contraction of the moisture during the cycling.

EXPERIMENTAL PROCEDURES

The material system selected for this study was a pultruded glass-reinforced polymer composite that utilizes a fire retardant isophthalic polyester resin with a UV inhibitor. This material system was chosen because of the large variety of structural shapes (e.g., tubes, channels, angles, I-shapes) that are currently manufactured from it. The material has a fiber volume fraction of 0.59 and an average density of 2048 kg/m^3 (0.074 lb/in^3). All samples used in the study were cut from 3.81-cm (1.5-in.) square stock.

As already noted, the purpose of this study was to determine the effects of moisture and low-temperature thermal cycling on the parallel-to-the-fiber notch toughness of the chosen material system. To that end, a test matrix was devised that would allow for two major test groups, DRY and WET, with each major group undergoing three levels of thermal cycling: 50, 150, and 300 cycles. A total of 90 specimens were prepared for this study: 15 specimens at each thermal cycle level for each major moisture group (15x3x2).

In this study, DRY refers to as-received specimens. The WET specimens reflect a 28-day water bath soak, with the corresponding 28-day moisture content ranging from 0.031 to 0.064 weight percent. The average 28-day moisture content of all specimens was 0.049 weight percent.

The test specimens were cut from square bar stock as shown in Figure 2(a). A diamond-tipped bandsaw blade was used to cut the specimens from the bar stock. The two faces at either end of the v-notch were machined for parallelism and the notch was made with a 90-degree end mill. The dimension from the base of the notch to the opposite side of the specimen was held to 1.143 ± 0.003 cm (0.450 ± 0.001 in.), see Figure 2(b). The length of the notch was 1.105 ± 0.003 cm (0.435 ± 0.001 in.), which was accomplished during the machining of the two faces for parallelism. The product of these two dimensions is the area of the specimen that resists the impact load. This cross-sectional area was determined for each specimen and the average value of 1.264 sq. cm. (0.1959 sq. in.) was used to normalize the impact energies as reported in Table 2. Based on the actual dimensions of the final specimens, the cross-sectional area of each specimen was within 0.5% of the average area noted above.

An MTS model 651 environmental chamber was used to thermally cycle the specimens between 25°C and −50°C. To ensure that the center of each specimen being thermally cycled reached the target temperatures, a temperature-monitoring specimen was made by drilling out the center of a specimen, inserting a thermocouple, and sealing with epoxy. The environmental chamber was then programmed based on the time-to-target temperature information obtained from the thermocouple. The specimens were held at the target temperature for one minute before reversing the thermal cycle.

To minimize the amount of moisture loss that the WET specimens may experience during the thermal cycling, each of the WET specimens was individually wrapped in polyethylene film (kitchen wrap), and the free edges taped. After completion of 50, 150, and 300 thermal cycles, specimens from the DRY and WET group were removed for testing and sealed in plastic bags. In addition, the WET specimens at 50 and 150 cycles that were to continue on with the thermal cycling were removed, weighed, and placed in a water bath for seven days. This was done in order to reproduce what occurs naturally in certain service environments (e.g., exposure to moisture – thermal cycles – exposure to moisture – thermal cycles – etc). After the weeklong water bath, these specimens were again weighed and wrapped prior to proceeding with the thermal cycling.

Upon completion of the thermal cycling the specimens were prepared for Izod testing. Of the fifteen specimens that made up each subgroup in this study, thirteen underwent Izod testing, and the other two specimens from each subgroup were set aside for cross-sectioning and crack density measurements. All Izod testing was performed at room temperature.

RESULTS

The weight of each of the WET specimens was measured at various points throughout the test program to monitor the moisture content in the material. From these measurements, the average percent weight gain, relative to the initial average specimen weight in the as-received condition, was determined at each step. These results are shown in Figure 3.

As can be seen from this figure, the specimens never reached a fully saturated state during the initial 28-day soaking period. Because of practical time considerations, the soaking was discontinued after 28 days with an average weight gain due to moisture of 0.049%. Following the initial soaking period, 50 thermal cycles were applied, followed by a 7-day resoak, another 100 thermal cycles, a 7-day resoak, and the final 150 thermal cycles. The average percent weight gain/loss due to moisture, relative to the as-received condition, is shown at the end of each of these events in Figure 3. As is evident, the specimens lost moisture during the thermal cycling, due to gradual evaporation and sublimation. It is of interest to note that the rate of moisture loss during cycling increased with the number of applied thermal cycles. During the first 50 cycles, the average moisture loss rate was 0.028 mg/cycle. By comparison, the loss rates during the next 100 cycles and final 150 cycles were 0.033 mg/cycle and 0.05 mg/cycle, respectively.

The increase in moisture loss rate with applied cycles may indicate an increase in internal damage in the composite due to the thermal cycling. The greater the extent of damage in the material (e.g., matrix cracks, voids, fiber/matrix debond cracks, etc.), the less resistance there would be to the migration of moisture from the interior to the surface of the specimen, where evaporation and sublimation take place. The two resoaking periods, after the first 50 and next 100 thermal cycles, replenished the lost moisture, although the second resoak was not sufficient to fully replace the moisture lost during the middle 100 thermal cycles. In addition, it should be pointed out that, after 300 thermal cycles, the WET specimens weighed less than they did in the “as-received” state, indicating that the material initially maintained a nominal moisture level prior to any soaking in water.

Following the application of 50, 150, and 300 thermal cycles, 13 specimens from each group (WET and DRY) were removed and impacted in an Izod test machine. The measured impact energies are shown in Table 2 and Figure 4. As can be seen, after 50 thermal cycles the average impact energy of the WET specimens was approximately 12% higher than that of the DRY specimens. After 150 thermal cycles, the DRY specimens showed almost no change, while the average impact energy of the WET specimens dropped by over 5%. After 300 thermal cycles, the difference in average impact energies between the WET and DRY specimens was negligible. Note that, in contrast to the previous results reported by the authors (Kellogg et al, 1999), there did not appear to be a significant increase in the scatter in the data for the WET specimens relative to the DRY specimens (except at 50 cycles). It is also worth noting that the trend of decreasing impact energy in the WET samples with increasing thermal cycles parallels the decrease in moisture content, as shown in Figure 3.

DISCUSSION

This study was conducted to better understand the effects of moisture and low-temperature thermal cycles on the Izod notch toughness of a pultruded, glass-reinforced composite. The authors initially hypothesized that if this material system contained moisture, repeated thermal cycles between room temperature and sub-freezing temperatures would result in a degradation of the notch toughness strength. This would be due to the increased size and number of cracks developing within the material, resulting from the expansion of the retained moisture when cooled below the freezing point. In addition, based on their previous study (Kellogg et al, 1999), the authors also speculated that WET specimens would initially have a higher mean notch toughness strength than the DRY specimens. This is the result of matrix swelling due to the absorbed moisture, which in turn reduces the internal residual stresses present from the manufacturing process. By reducing the internal residual stresses, the notch toughness strength is increased. It was further believed that the initial benefits of absorbed moisture would be counteracted by the increasing number and size of cracks developing as the number of thermal cycles increased, eventually reaching a point where the detrimental effects of increased crack density would negate the beneficial effects of moisture. The results of this study support some of the aforementioned hypotheses and also offer some interesting findings.

To ensure that the thermal cycling of WET specimens did not reproduce the effects of thermal cycling of DRY specimens, the WET specimens were repeatedly exposed to moisture. This condition is necessary because of two phenomena. First, once expanding moisture has increased the volume of a crack within the material to that of the frozen water, subsequent cooling cycles will do little to increase the size of existing cracks. Second, specimens may lose moisture during thermal cycling due to evaporation and sublimation, resulting in WET specimens that start to resemble DRY specimens.

An indicator that the size and/or number of cracks within the material is increasing is shown in Figure 3. Notice that during the initial 50 thermal cycles, the rate of moisture loss is not as great as during the next 100 thermal cycles. In the final 150 thermal cycles, the specimens lost moisture at an even faster rate. This can be attributed to the fact that as the size and/or number of cracks increase, the ability of the material to readily absorb or lose moisture also increases. The authors are currently conducting experiments on the specimens to determine the actual change in internal crack size and density with increasing thermal cycles so as to quantify the above statement.

The results of this study also indicate that absorbed moisture has a beneficial effect on the notch toughness strength. Referring to Figure 4, the mean notch toughness of the WET specimens in this study is higher than the DRY specimens at all cycle levels except at 300 thermal cycles, where they are almost identical. At the completion of 50 thermal cycles and 150 thermal cycles, the WET specimens still had moisture levels above the reference state (zero days in Figure 3). At the end of 300 total thermal cycles, the specimens had lost all of the moisture gained during the soak phases plus some residual moisture from the as-received condition. In describing this behavior it is believed that two mechanisms may be at work here. The first mechanism is the reduction of internal residual stresses due to absorbed moisture in the matrix. The second mechanism is dependent upon the extent of the internal cracking due to thermal cycling. Low levels of internal cracking may be beneficial by reducing the internal residual stresses, thus increasing the notch toughness. High levels of internal cracking would be detrimental to the notch toughness due to vast discontinuities and voids within the material. It is estimated here that the degree of internal cracking for these specimens is at a low level, as the mean notch toughness of the WET specimens after 300 thermal cycles is only slightly below that of the DRY specimens. This seems plausible as both WET and DRY specimens have essentially the same moisture content after 300 thermal cycles. As already stated, the authors are currently conducting cross-sectioning experiments to quantify the extent of internal cracking within these specimens.

SUMMARY AND CONCLUSIONS

Notched Izod impact tests were conducted on wet (soaked in water) and dry specimens of a pultruded, glass fiber reinforced polymer composite after thermal cycling between 25 and –50ºC. Thirteen specimens, at each moisture state, were impacted following the application of 50, 150, and 300 thermal cycles, with the wet specimens undergoing a resoak period after 50 and 150 cycles. The specimens were oriented such that the direction of impact was parallel to the fibers. The wet specimens were also weighed periodically to track the moisture levels during the test program.

The results of the study indicate a beneficial effect from moisture initially, which is likely caused by a reduction in residual stresses due to swelling of the matrix. This benefit, which was also observed by the authors in a previous study (Kellogg et al, 1999), is evidenced by an increase in the notch toughness of the wet specimens, relative to the dry specimens, after application of 50 and 150 thermal cycles. However, after 300 thermal cycles, the mean notch toughness of the wet specimens had dropped to a value roughly equal to that of the dry specimens. It is believed that there are two mechanisms that contribute to this behavior: an increase in the extent of internal damage in the composite due to the expansion and contraction of the moisture during freeze/thaw cycling, and a reduction in the overall moisture state in the composite due to evaporation and sublimation. Cross-sectioning of specimens is currently being conducted in an attempt to quantify the accumulation of damage in the composite during thermal cycling.

TABLES AND FIGURES

Table 1
Notched Izod Impact Energy (N-m/cm^2) for a
Pultruded Glass Fiber Composite (Kellogg et al, 1999)

Temp. (ºC)	Dry Mean	Dry Range	Wet Mean	Wet Range
25	0.341	0.201 - 0.510	0.392	0.270 - 0.646
–5	0.351	0.285 - 0.484	0.351	0.211 - 0.593
–25	0.345	0.275 - 0.463	0.367	0.238 - 0.600
–50	0.414	0.279 - 0.530	0.448	0.280 - 0.658

Table 2
Notched Izod Impact Energy (N-m/cm^2) for a
Pultruded Glass Fiber Composite after Thermal Cycling

Condition	Thermal Cycles	Mean	Standard Deviation	Range
Dry	50	0.481	0.054	0.397 - 0.59
	150	0.482	0.055	0.397 - 0.579
	300	0.502	0.087	0.376 - 0.697
Wet	50	0.539	0.080	0.429 - 0.665
	150	0.509	0.051	0.456 - 0.622
	300	0.492	0.081	0.386 - 0.665

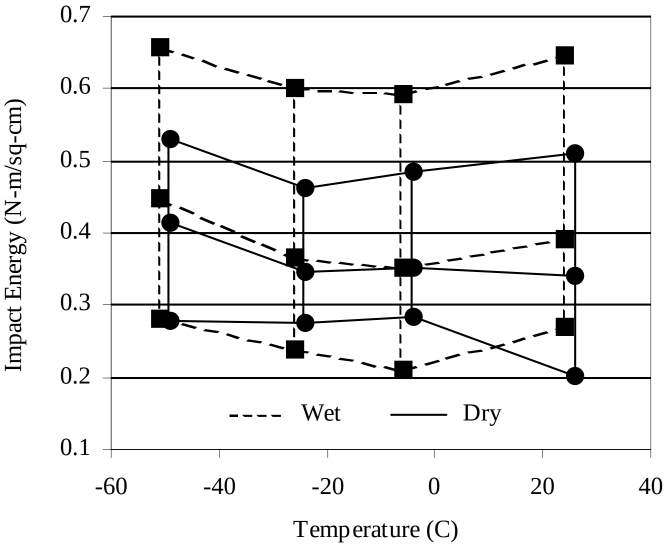

Fig. 1 Results of Izod notch toughness experiments (high-avg-low) (Kellogg et al, 1999).

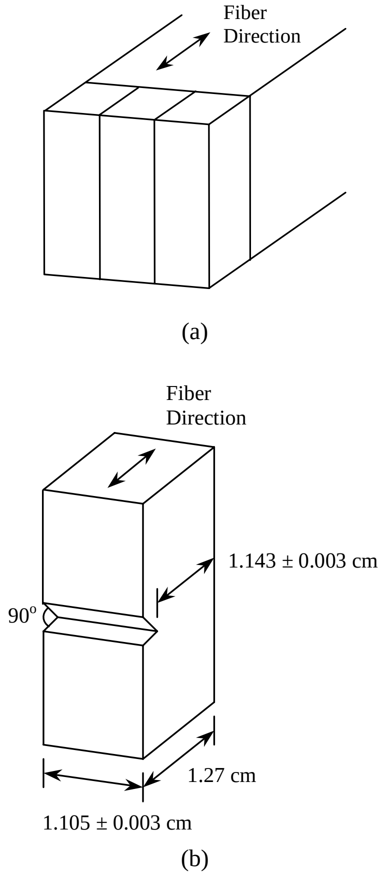

Fig. 2 (a) Specimen extraction from solid bar stock, and (b) specimen geometry.

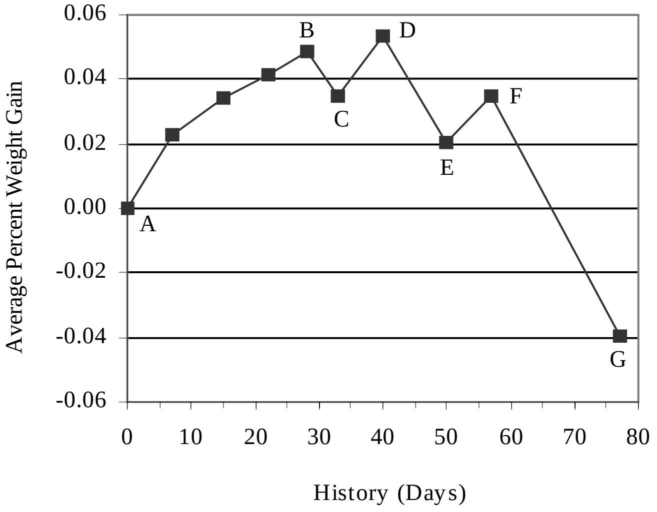

Fig. 3 Average percent weight gain due to moisture in the WET composite specimens during the test program (A: start initial 28-day soak. B: end 28-day soak, start 50 thermal cycles. C: end 50 thermal cycles, start 7-day resoak. D: end 7-day resoak, start 100 thermal cycles. E: end 100 thermal cycles (150 total), start 7-day resoak. F: end 7-day resoak, start 150 thermal cycles. G: end 150 thermal cycles (300 total)).

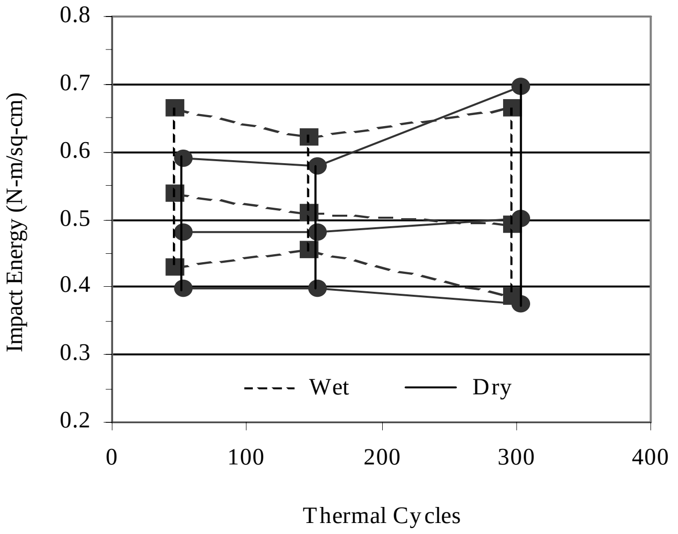

Fig. 4 Results of Izod notch toughness experiments after thermal cycling (high-avg-low).

REFERENCES

Dutta, PK, Faran, KJL, and Hui, D (1993). “Influence of Low Temperature on Energy Absorption in Laminated Composites,” *Composites Behavior*, ICCM/9 Proceedings, A Miravete, Ed., pp. 311-320.

Dutta, PK, McDevitt, CF, and Manikonda, SG (1994a). “Applications of Recycled Plastics for Roadside Safety Hardware,” *Materials and Design Technology, PD-Vol. 62*, ASME, pp. 345-349.

Dutta, PK, Kumar, MM, and Hui, D (1994b). “Dynamic Tensile Strength of Glass Fiber Reinforced Pultruded Composites,” *Materials and Design Technology, PD-Vol. 62*, ASME, pp. 357-363.

Karbhari, VM, and Pope, G (1994). “Impact and Flexure Properties of Glass/Vinyl Ester Composites in Cold Regions,” *Journal of Cold Regions Engineering*, Vol. 8, No. 1, pp. 1-20.

Kellogg, KG, Kallmeyer, AR, Chinman, RB, and Dutta, PK (1999). “Influence of Moisture and Low Temperature on Notched Izod Impact Toughness in a Pultruded Reinforced Composite,” *Proceedings, Ninth International Offshore and Polar Engineering Conference*, Brest, France.

Nishijima, S, and Okada, T (1982). “Charpy Impact Test of Cloth Reinforced Epoxide Resin at Low Temperature,” *Nonmetallic Materials and Composites at Low Temperatures*, G Hartwig and D Evans, Eds., Plenum Press, New York, pp. 259-275.

Russell, AJ, and Street, KN (1985). “Moisture and Temperature Effects on the Mixed-Mode Delamination Fracture of Unidirectional Graphite/Epoxy,” *Delamination and Debonding of Materials, ASTM STP 876*, WS Johnson, Ed., American Society for Testing and Materials, Philadelphia, pp. 349-370.

Voelker, MJ (1991). “Low Temperature Impact Properties of Long Fiber Thermoplastic Composite Molding Materials,” *Polymer Composites*, Vol. 12, No. 4, pp. 119-121.

Wigley, DA (1971). *Mechanical Properties of Materials at Low Temperatures*, Plenum Press, New York, p. 24