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Benefits of Surface Coatings for Impacted Composites for Cryogenic Tankage

Benjamin C. Findley* and W. S. Johnson†
Georgia Institute of Technology, Atlanta, Georgia 30332-0245

NASA intends to use composite materials for both fuel tanks and fuel feedlines on future generations of reusable launch vehicles in an effort to reduce the overall vehicle weight, which in turn increases the weight of payload that can be sent into orbit. Composite feedlines have been found to be vulnerable to impacts (dropped tools and accidental bumps, etc.). Because composites dissipate impact energy through the formation of damage, it was necessary to determine whether polymeric coating materials could be used to improve the composite's resistance to impact, and also whether these same coatings could prevent fuel permeation through any damage that would result from these impacts. Furthermore, many polymeric materials continue to embrittle with time, and so the effects of aging were studied. Finally, thermal cycling of the coated composite specimens was performed to simulate the conditions present in launch-to-landing cycles.

Introduction

COMPOSITE materials are being considered for use on future generations of reusable launch vehicles (RLVs) in an effort to reduce the overall vehicle weight. It is hoped that for the second-generation RLV the cost per pound of payload can be reduced from \$10,000 to \$1000, and then to \$100/lb for third-generation vehicles.[1] It is estimated that simply by switching to composite materials for fuel tanks the weight of the tank can be reduced 40%, which translates to a savings of 14% in total vehicle weight.[2]

Composite fuel feedlines are vulnerable to low-velocity impact events. Because composite materials dissipate impact energy through the formation of damage, which could lead to fuel leakage, these impacts are of particular concern.

Composites initially dissipate impact energy through the formation of cracks in the matrix material. These cracks can then lead to delaminations between plies of different orientations, and even to broken fibers.[3–6] Damage need not be visible in a composite for leakage to result.[7] Using a drop-weight impact test machine, Nettles found that impacts with as little as 1.07 J could cause enough damage in woven four-ply carbon/epoxy composites for leakage to occur. That energy is equivalent to the impact energy of a 110-g mass dropped from only 1 m.

Cryogenic feedlines and fuel tanks are exposed to wide temperature ranges (20–400 K), which can lead to damage in the composite. Microcracking of the matrix occurs at temperatures below 60 K, and after only a few cycles, this microcracking will reach the maximum crack density.[8]

In addition to the risk of impact, it has been found that some of the sample feedlines produced have actually had leakage before any impact events whatsoever. Therefore, it is necessary to determine whether there is a method of repair that will allow leaking feedlines to be salvaged.

Acceptable rates of permeation for both liquid oxygen and liquid hydrogen are extremely low. (For the purposes of this research any identifiable leaks were considered impermissible.) Because fuel leakage may occur through damage invisible to the naked eye, the composite's impact resistance must be improved.

This research investigates the potential of coatings to improve the impact resistance of carbon/epoxy composites to be used for fuel feedlines and cryogenic tankage on future RLVs. These same coatings were also tested to determine whether they could be used to repair composites with preexisting leaks. The testing in this research accomplishes this goal through use of a drop-weight impact test machine in conjunction with a basic leak detection apparatus that can also be used to quantify the rate of gaseous permeation through any leaks. Developing durable impermeable composites is vital if these materials are to be used for cryotankage on future RLVs.

Experimental Techniques

All of the composite specimens tested in this research were made from woven IM7 carbon fibers in a matrix of EX1552 (a toughened epoxy). The specimens were cut from 1×1 m four-ply panels processed at NASA Marshall Space Flight Center (MSFC), with a $[0/90]_4$ layup. The panels were laid up and autoclaved according to the manufacturer's specifications. These materials are typical of those being considered by NASA for use on fuel tanks and feedlines of future RLVs.

Several different commercially available coating materials were considered in this project. An emphasis was placed on testing different polyurethane materials because of both their toughness and also their low permeability. Three different polyurethane materials were considered, an aliphatic moisture curing polyurethane, a polyurethane material reinforced with micaceous iron oxide and aluminum (MIO–Al) particles, and a polyester aliphatic urethane. Additionally, a thermoplastic coating was considered, Thermoflex II-C, because it was marketed as being highly impact resistant with low permeability.

Specimen Screening

In this project, more than 250 specimens were received, and it was necessary to screen them all. Every specimen received was tested for leakage and classified based on the number of leaks present. Specimens found to have three or more leaks were set aside to test the ability of coating materials to seal preexisting leaks. Specimens that leaked initially, but were found to be impermeable after being coated, were tested to find the critical impact energy (maximum impact energy that a composite can withstand before developing leakage) of the coated specimen. Some of the specimens with no leaks were used to find the baseline critical impact energy, whereas the others were coated and impacted to find the improvement factor (critical impact energy with coating divided by the value without a coating) for each coating material.

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*M.S.M.E. Student, Mechanical Engineering and Materials Science and Engineering.
†Professor, Mechanical Engineering and Materials Science and Engineering.

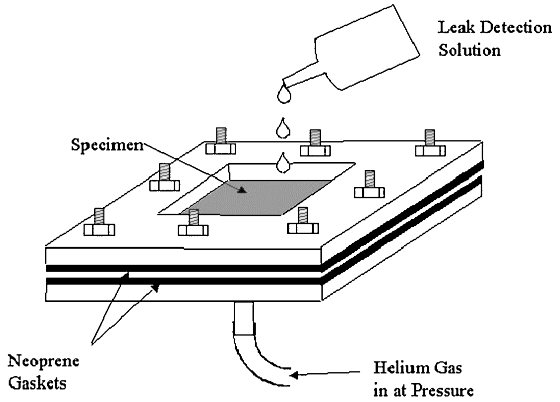


Fig. 1 Leak detection apparatus.

Coating Application

All of the specimens that were to be coated had to be thoroughly cleaned to remove residual vacuum grease before the application of the coatings. Each specimen was wiped down with acetone several times and then lightly abraded with 360-grit sandpaper and wiped down again. Weight and thickness measurements were taken for all specimens before and after coating application.

Because composites are being used to reduce the vehicle weight, it is important that the coatings be applied as thinly and uniformly as possible. All coatings were applied by brush. The polyurethane materials were applied in two coats, with the second coat being applied at least 24 h after the first. The thermoplastic materials were applied in the same manner, but three coats were needed to achieve uniform and complete coverage. In both cases, prior coats were not sanded before the next coat was applied.

Leak Testing

All specimens had to be screened for leakage before any could be impacted or coated. Furthermore, those specimens that had three or more leaks before being coated had to be leak tested again after coating, before they could be impacted. All of the leak testing that was done in this research was done using an apparatus very similar to one used at NASA MSFC, shown in Fig. 1.[9]

In this test, a specimen is sandwiched between two gaskets, which are in turn sandwiched between two aluminum plates. The bottom plate has a chamber to which helium gas is applied at pressure. The top plate has a hole, which is filled with a soap and water solution. Any leaks in the specimen will appear as a stream of bubbles.

Impact Testing

All impact testing done in this research had to model impacts caused by accidental bumping of the feedlines or impacts from dropped tools. For this reason, a drop-weight-type impact test machine was used. Nettles found that these types of impact are best modeled using a blunt impactor[7]; thus all testing was done with a 1.27-cm (0.5-in.) hemispherical tup.

It was necessary to find the critical impact energies of 1) the initially impermeable uncoated specimens, 2) the coated initially impermeable specimens, and 3) the initially leaking then coated specimens. To do this, specimens were impacted and then leak tested. The impact energy was then either increased or decreased as necessary.

Permeability Testing

Those specimens that leaked following impact were tested to quantify the rate of permeation through the impact damage. This was done to show how leakage develops in the coated composite systems with increasing impact energies.

All permeability testing was done using a device derived from the volumetric approach outlined in American Society for Testing and Materials (ASTM) standard D1434.[10] In this test, a specimen would be sandwiched between two gaskets, which are in turn placed between two identical aluminum plates. The bottom plate has a chamber to which helium gas can be applied, whereas the top plate has a chamber that funnels any permeating gas into a tube that contains a slug of isopropyl alcohol. The rate of permeation is determined by measuring how far the alcohol slug moves up an inclined glass tube in a certain amount of time.

Specimen Aging

Many polymeric materials embrittle with time. Because impact resistance is largely a function of polymer ductility, it was important to test for the effects of aging. Two of the initially leaking specimens were coated with each material and then set aside for aging. Specimens were aged for four months in a room temperature and humidity environment (approximately 24°C and 50–80% humidity). Specimens were impacted at the critical impact energies and then tested for leakage. If the polymer was more brittle following the aging, then impacts at the critical impact energy should cause leakage.

Thermal Cycling

The composite fuel tanks and feedlines will experience extremely large thermal cycles during every flight. During a typical flight cycle, a feedline will start at the cryogenic fuel temperatures (20 K), then during reentry be heated to 400 K, and then at landing and during storage to 300 K (Ref. 2). These large temperature changes result in tremendous stresses in both the composite and the coating.

Coating materials have been found to be prone to delamination at cryogenic temperatures, and so it was necessary to perform thermal cycling testing on the coated specimens. Damage caused by thermal cycling into the cryogenic range accumulates quickly, with the maximum crack density of carbon/epoxy composites generally being reached within five cycles.[2]

Coated specimens, that initially had three or more leaks, were thermally cycled five times from room temperature, to 77 K (liquid nitrogen), back to room temperature, and then to 394 K. Liquid nitrogen was used for the cryogenic portion of the testing because there is published research that indicates that coatings tend to delaminate by 77 K. Other researchers have found that damage in the composite will not initiate until 60 K (Ref. 11). Thermally induced damage in the composite, although a significant concern, was not the primary focus of this research; achieving a viable composite-coating system was. Thus, liquid nitrogen was used for thermal cycling instead of liquid helium. Following the thermal cycling, all of the specimens were tested for leakage. The test progression is given in Table 1.

Results

Coatings

As already mentioned, all of the coatings were applied by brush. This resulted in some variation in the thickness and evenness of the coatings themselves. Also, because composites are being used to save weight, it is of the utmost importance that the coatings applied not undermine this weight savings. Table 2 shows the average thickness, weight added, and percent increase in weight of the specimen due to the coatings for the specimens that initially had three or more leaks. Table 3 shows the same data but for the specimens that initially had no leaks.

Impact Test Results

Table 4 shows the critical impact energies that were found for the specimens that initially had three or more leaks, as well as the improvement factor that was provided by the coating over the initially impermeable uncoated specimen. The improvement factor is simply defined as the critical impact energy of the coated specimen divided by the critical impact energy of the initially impermeable uncoated specimen. Table 5 shows the same data but for the specimens that had no leaks before being coated.

Effects of Aging

Two specimens that initially had three or more leaks were coated with each of the different materials and aged for four months in a room temperature and humidity environment. After impacting each of these specimens, with the relevant impact energies, only two

Table 1 Test progression

Order	Status	Tests performed
1	As received	Leak test, then sorted according to number of leaks present
2	Initially impermeable, uncoated	Impacted, then leak tested to find the critical impact energy
3	Initially impermeable, then coated	Leak tested; if no leaks found, then impacted and leak tested again (finding critical impact energy). Those that leaked after impact were tested to find the rate of permeation.
4	Initially leaking, then coated	Leak tested; if no leaks found, then impacted and leak tested again (finding critical impact energy). Those specimens that leaked were tested to find the rate of permeation
5	Aged initially leaking, then coated	Leak tested; those that did not leak were then impacted at the relevant critical impact leak tested energy, and again
6	Initially leaking, then coated	Leak tested; if no leaks found, then thermally cycled and leak tested again. If no leaks were found, then impacted and leak tested again.

Table 2 Additional thickness and weight from coatings on carbon/epoxy specimens that initially had three or more leaks

Coating	Coating weight, N/m^2 (lb/ft^2)	Average coating thickness, cm (in.)	Additional weight, %
Moisture curing aliphatic polyurethane	3.45 (0.072)	0.023 (0.009)	1.2
Polyurethane with MIO–Al particles	2.58 (0.054)	0.015 (0.006)	0.84
Polyester aliphatic urethane	3.78 (0.079)	0.025 (0.010)	1.34
Thermoplastic	6.70 (0.140)	0.051 (0.020)	2.82

Table 3 Additional thickness and weight from coatings on carbon/epoxy specimens that were initially impermeable

Coating	Coating weight, N/m^2 (lb/ft^2)	Average coating thickness, cm (in.)	Additional weight, %
Moisture curing aliphatic polyurethane	3.59 (0.075)	0.023 (0.0089)	1.28
Polyurethane with MIO–Al particles	2.54 (0.053)	0.017 (0.0066)	0.95
Polyester aliphatic urethane	2.87 (0.060)	0.018 (0.0071)	1.02
Thermoplastic	5.79 (0.121)	0.047 (0.0187)	2.7

Table 4 Critical impact energies for the coated carbon/epoxy specimens that initially had three or more leaks

Coating	Critical impact energy, J (ft · lb)	Improvement factor
None	1.07 (0.79)	NA
Moisture curing aliphatic polyurethane	5.90 (4.35)	5.51
Polyurethane with MIO–Al particles	4.31 (3.18)	4.03
Polyester aliphatic urethane	5.25 (3.87)	4.90
Thermoplastic	3.12 (2.30)	2.91

Table 5 Critical impact energies for the coated carbon/epoxy specimens that initially had no leaks

Coating	Critical impact energy, J (ft · lb)	Improvement factor
None	1.07 (0.79)	NA
Moisture curing aliphatic polyurethane	5.15 (3.80)	4.81
Polyurethane with MIO–Al particles	3.80 (2.80)	3.54
Polyester aliphatic urethane	5.11 (3.77)	4.77
Thermoplastic	3.20 (2.36)	2.99

Table 6 Results of leak testing on aged specimens impacted with the relevant critical impact energy

Specimen	Coating	Leakage notes
X-24	Moisture curing aliphatic polyurethane	1 Leak at 172.4 kPa (25 psi)
G-9	Moisture curing aliphatic polyurethane	No leaks
X-57	Polyurethane with MIO–Al particles	No leaks
X-26	Polyurethane with MIO–Al particles	No leaks
X-70	Polyester aliphatic urethane	Delamination formed at 137.9 kPa (20 psi)
H-7	Polyester aliphatic urethane	No leaks urethane
F-10	Thermoplastic	No leaks
X-80	Thermoplastic	No leaks

leaked (one moisture cured aliphatic polyurethane and one polyester aliphatic urethane). Table 6 shows the results of the leak testing on the specimens that were aged.

Discussion

More than 250 specimens were received during this research, of which 24% had no leaks, 36% had one or two leaks, and 30% had three or more leaks. To get an accurate assessment of whether or not coatings could seal preexisting leaks, it was necessary to test specimens that had extensive leakage. For this reason, specimens that had only one or two leaks were not used. The variability in number of leaks in the specimens is a function of the tremendous inconsistency found in the composite material. From C scans performed at NASA Langley Research Center, it was found that there was a wide variation in the consolidation and density of the specimens. Figure 2 shows the results of a C scan on a typical specimen. The dark areas represent regions with greater density and consolidation, and the lighter areas represent voids and poorly consolidated regions in the composite.

Some tensile testing was performed on the materials received, per ASTM standard D3039,[12] and again the variability of the material was evident. The ultimate tensile strength of the composite was found to vary from 740 to 950 MPa, and the modulus varied from 20,400 to 30,300 MPa.

Coatings

One can see that through the use of a coating, significant improvement could be made in the impact resistance of carbon/epoxy composites. The moisture-cured aliphatic polyurethane tested in this research not only was the easiest to apply but also provided the greatest improvement in impact resistance. Note that both the polyester aliphatic urethane and the thermoplastic coatings tended to fail by delaminating from the composite substrate when helium was applied. The moisture-cured aliphatic polyurethane tended to show visible signs of failure when the critical impact energy had been exceeded. Frequently, there would be cracking in the coating near the indentation left by the impactor. The MIO–Al polyurethane did not always show any visible signs of damage, but this could be due to the surface finish of the coating, which was generally rough.

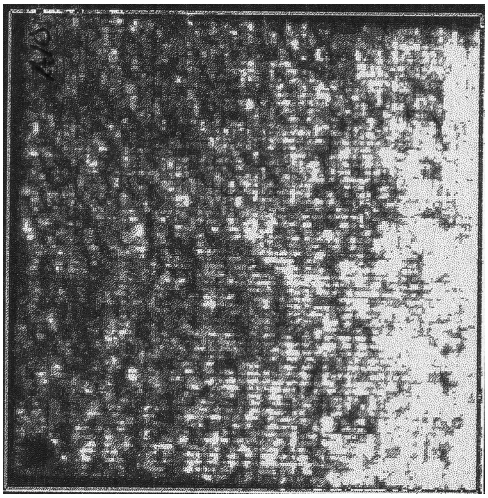


Fig. 2 C scan of a typical specimen.

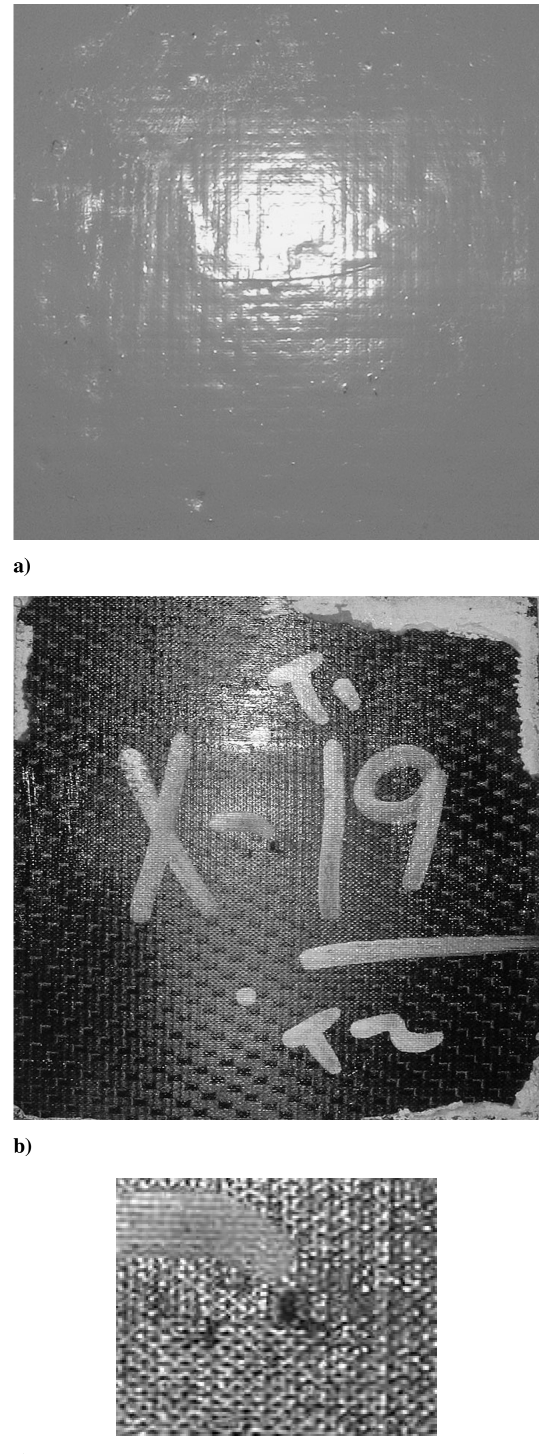


Fig. 3 Moisture-cured aliphatic polyurethane-coated specimen impacted at 4.35 ft · lb (5.90 J): a) indentation in front side of specimen, b) back of specimen, and c) closeup of damage on back of specimen.

From the data in Tables 4 and 5 it is evident that sealing preexisting leaks with coatings is a viable method of repairing leaking specimens. The sealed initially leaking specimens actually outperformed the coated initially impermeable specimens, which was unexpected. It is suspected that the reason for this behavior is twofold. First, the coatings applied to these specimens were a little thicker on average. This increased the moment of inertia of the specimens slightly, but more importantly presented more elastic material to absorb impact energy. Second, it is suspected that the specimens from the initially impermeable set may have been some of the ones that were not as thoroughly cured and, thus, were weaker.

It was expected that through the application of polymeric coatings the impact resistance would be improved. Damage would still occur in the composite, but the coatings are sufficiently ductile to remain intact even when the composite cracked, thus eliminating any leakage. On inspection of the impacted specimens, it became clear that the coatings significantly reduced the amount of damage that formed in the composite. Some of the reduction in damage is certainly due to impact energy being dissipated through elastic deformation of the coating, but it is also possible that just by increasing the cross section of the composite slightly the flexural properties change. Figures 3 and 4 show two specimens that were impacted at the same energy. The specimen in Fig. 3 was coated with the moisture cured aliphatic polyurethane, whereas the specimen in Fig. 4 was not coated at all.

The weight added by the coating materials was generally small, at most an increase of less than 3%. Also, note that the thickness of the coatings varied, with the specimens that had three or more leaks generally having slightly thicker coatings. Coating thickness effects were evident in the comparison between the impact test results of the specimens that initially had three or more leaks and those that were initially impermeable.

Before impacting any of the specimens, all of the coated specimens were leak tested to ensure that all were impermeable. None of the sealed specimens leaked, and so all were included in the impact testing.

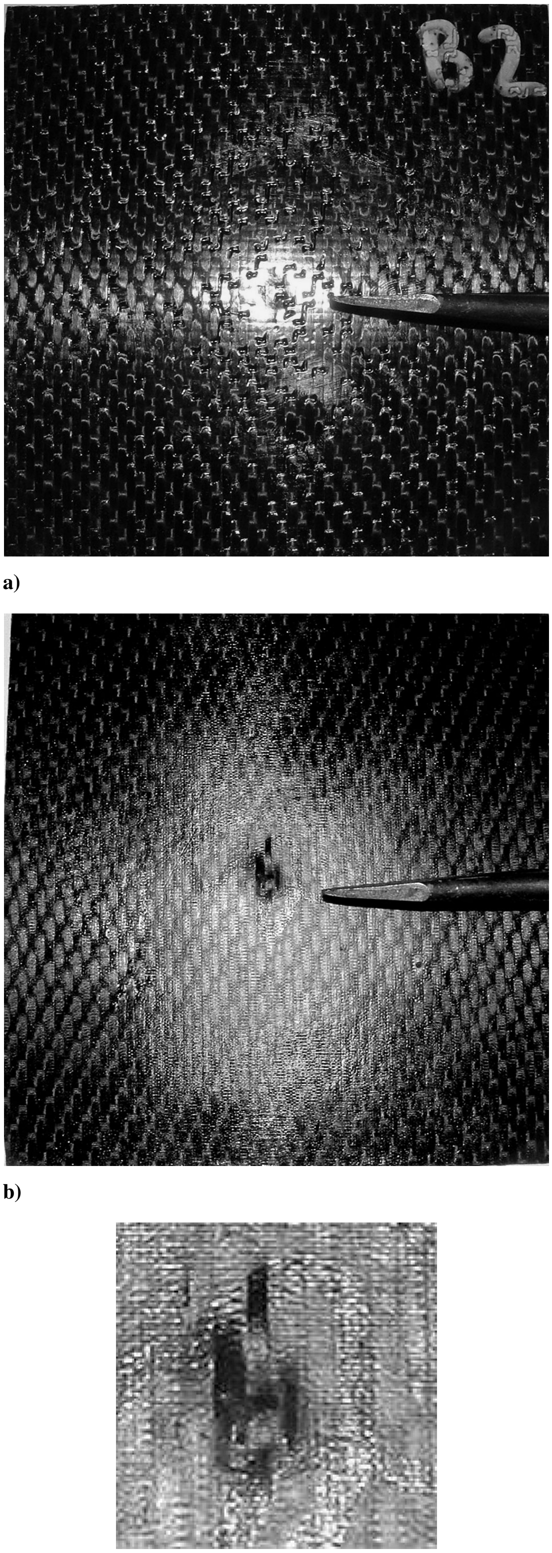
Effects of Aging

Although two specimens did leak, it is suspected that this may be due to the variability of the coating application and/or the composite substrate. It was expected that if the coatings had become more brittle with age then more of the specimens would have leaked. Also, because of the variable nature of the specimens, it was impossible to be certain that aging had any effect. The fact that at least one specimen coated with each material showed no embrittlement supports the assertion that the two failures may not be effects of aging. However, to be sure, this testing would have to be repeated with a larger sample size.

Thermal Cycling

Two specimens coated with each material, all initially with leaks, were put through five thermal cycles (ranging from 77 to 394 K). After only two cycles, the thermoplastic coating had completely failed. It had extensive cracking over the entire surface area and also was actually peeling away from the composite substrate. Figure 5 shows the thermoplastic specimen after two thermal cycles.

The polyester aliphatic urethane coated specimens did not perform much better. After only three thermal cycles, the topcoat of the urethane had almost completely delaminated from the base coat. This phenomenon is shown in Fig. 6.



a)

b)

c)

Fig. 4 Uncoated specimen impacted at 4.35 ft · lb (5.90 J): a) front of specimen, b) back of specimen, and c) closeup of damage on back of specimen.

The moisture-cured aliphatic urethane-coated specimens performed better in thermal cycling; nevertheless, after several cycles, hairline cracking was visible on the surface of the coating. By the end of the fifth cycle, the cracking covered all of one specimen and approximately half of the other specimen.

The polyurethane with MIO–Al particles showed no visible signs of damage following the five complete thermal cycles. On leak testing, though, these specimens had many leaks. Other researchers,

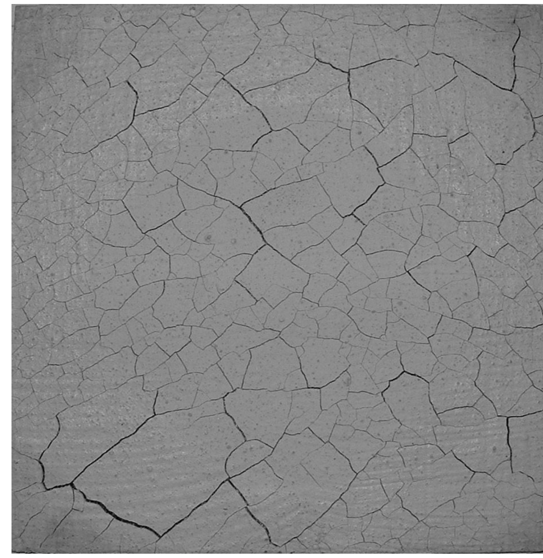


Fig. 5 Thermoplastic-coated specimen after two complete thermal cycles.

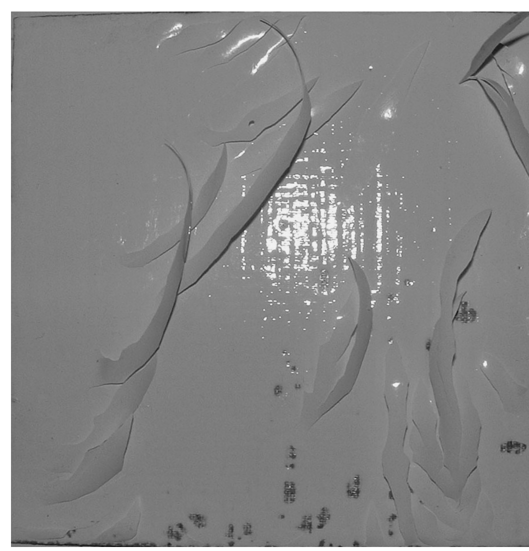


Fig. 6 Polyester aliphatic urethane-coated specimen after three thermal cycles.

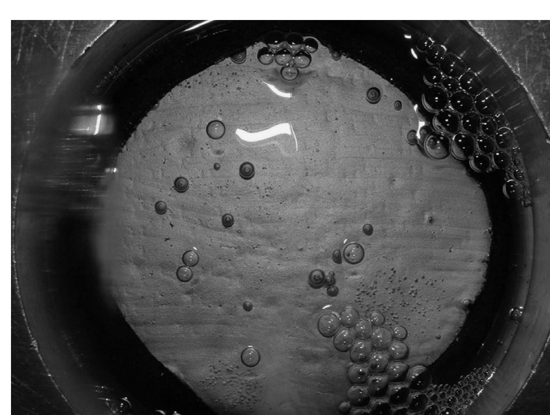


Fig. 7 Specimen coated with the polyurethane with MIO–Al particles being leak tested after thermal cycling.

particularly LeBaron et al.,[13] note that with nanocomposites one has the ability to adjust the coefficient of thermal expansion (CTE). It is believed that by adjusting the amount of microscale or nanoscale reinforcement in a polymer one could more closely match the CTE of the composite substrate. This would result in lower thermal stresses and, thus, a lower propensity for the coating material to crack or delaminate from the composite.

Despite what Kessler et al.,[2] Nettles,[7] and others have found, damage appeared to form in the carbon/epoxy composite at temperatures above 60 K. Both of the specimens coated with the polyurethane with MIO–Al particles initially only had three leaks; yet after thermal cycling, many more leaks were found. This suggests that damage actually initiated throughout the material. Figure 7 shows a specimen coated with the polyurethane with MIO–Al particles being leak tested after thermal cycling. The bubbles are different leaks.

Conclusions

This research has shown that polymeric materials can be used to improve the impact resistance of carbon/epoxy materials significantly (in this case as much as a 5.5-fold improvement). Aging of the polymeric coatings was found to have little or no effect, but this was with both small sample sizes and with aging periods of only a few months. This is a subject that probably requires further consideration.

In cryogenic environments, all of the materials tested failed. It is believed that the polyurethane with MIO–Al particles demonstrated the promise of microscale or nanoscale reinforced materials for cryogenic applications. This material survived thermal cycling without visible damage, which suggests that there may have been less damage present in this coating compared to the other materials.

Because this research effort primarily focused on improving the impact resistance of the composite, too much emphasis was placed on finding coatings with desirable characteristics for impact resistance and not enough on achieving a composite-coating system with sufficiently similar CTEs. Future work must put greater emphasis on CTE compatibility. In particular, performing CTE testing before coating selection would be advised.

Aside from these shortcomings, this research has demonstrated the viability of coatings as a means of improving the impact resistance of composites, as well as a method of sealing existing damage. Furthermore, the impact and permeability test method used in the research proved to be both a simple and effective assessment of coatings for use with composite fuel lines.

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D. Edwards
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