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Polymer Matrix Composite Manufacturing Induced Defects

INTRODUCTION

Polymer matrix composites (PMCs) comprise more than 90% of the composite materials available. They are used extensively within industry and the DoD due to their high stiffness and strength, low density, long fatigue life, corrosion resistance, and crash worthiness.[1, 2] These materials can also be tailored to exhibit stealth characteristics, sensor capabilities, and high thermal or electrical conductivity.[3]

With many desirable properties, the potential applications for PMCs continue to increase. As a result, it is becoming ever more important to know, and have a basic understanding of, the underlying causes for polymer matrix composite (PMC) material failure, specifically those that result from the manufacturing process since it accounts for approximately 44% of the failures in [fiber-reinforced] PMCs.[4] These failures result from defects that are inherently introduced during the manufacturing process, either from the reactions that occur within the resin during material processing, or via mechanical, human, or environmental factors. This article surveys the common defects that result from the manufacture of PMCs.

BACKGROUND

Polymer matrix composites consist of matrices made of polymeric materials*, such as plastics† or resins‡ that are either thermosetting or thermoplastic, and fibrous reinforcements.[1] The reinforcements (e.g., natural, oxide glass, aramid, or carbon or graphite fibers) can be placed in any direction and used in a variety of shapes and sizes (i.e., straight and continuous; discontinuous or chopped; particles or flakes; or continuous and woven, braided, or knitted).[2] The continuous matrix provides form to the much stiffer and stronger reinforcements, distributes loads across the reinforcements, and protects the reinforcements from the environment and weathering.[1, 2]

Thermosetting resins are liquid at room temperature. As the name implies, thermosetting resins solidify with heat in a process known as curing. The heat from the curing process creates cross links between the single and branched polymer chains of the resin to create a solid 3-dimensional (3-D) structure. Since voids are inherently introduced during the cure process, PMCs are typically debulked§ to reduce the void content.[1] Once cured, the component is cooled to its service temperature.[1, 5]

Thermoplastic resins, on the other hand, are solid at room temperature.[1] These resins are heated to a processing temperature above the melting point, molded, and solidified upon cooling to the service temperature.[6] This cooling process causes the matrix to shrink, creating Van der Waals bonds between the fibers and the matrix.[9] Table 1 compares the common attributes of thermoset and thermoplastic matrices. Table 2 provides an overview of the basic PMC manufacturing methods.

Table 1. Comparison of thermoplastic and thermoset matrices.[2, 5]

Thermoset Resins	Thermoplastic Resins
• Develop well-bonded 3-D structures	• 1-D or 2-D in molecular structure
• Do not melt once hardened	• Soften at high temperatures, showing a discrete melting point
• Require a curing process	• Become rigid with cooling
Uncured resins are susceptible to moisture and temperature effects, and contamination	• Examples: polyethylenes, polyesters, polyketones, polysufones, polypropylenes, polyamides
Under-cured resins are too soft to transmit loads efficiently between the matrix and the fibers	• Can be crystalline or amorphous
Over-cured resins become embrittled and crack prematurely	• Creep is a concern, but can be minimized with the proper reinforcement selection
• Can be left in a partially cured state	• No chemical reactions are needed, thus no excess heat or product gas are released
• Most often used in chopped fiber composites	• The limiting factors in production are time to heat, shape, and cool
• Examples: Epoxies, unsaturated polyesters, phenolics, vinylesters, bismaleimides	• Materials can be salvaged and re-worked
• Commonly used for aircraft, space, military, and automotive parts	• Lose strength at high temperatures
• Produced by condensation polymerization or by addition polymerization, followed by a condensation rearrangement reaction to form heterocyclic entities	
Both produce water, making it difficult to produce void-free parts or structures	

Table 2. Overview of the basic polymer matrix composite manufacturing methods. These methods apply to both resin types; however, different considerations must be included for each.[1, 2, 7, 8]

Manufacturing Method	Description
Hand Lay-up	Reinforcing fibers are placed in the mold (after a release film and gel coat in some instances); the resin material is then rolled into the reinforcing fibers. Hand lay-up is commonly used in the US aircraft industry to produce PMC parts.
Spray Lay-up	The reinforcements are chopped and sprayed simultaneously with the resin into the mold. A roller is then used to ensure that the resin fully wets the fiber bundles. This technology produces low specific strength structures and is used to join back-up structures to composite face sheets on composite tools.
Manual Prepreg** Lay-up	The prepreg is cut into several layers, as needed for the mold. The shaped prepregs are then layered within the mold.
Automatic Prepreg Lay-up	(Applicable to flat panels or parts with moderate curves.) A tape-laying machine lays the prepreg in the mold, cutting the prepreg when the mold edge is reached. This process is repeated until the part is complete.
Compression Molding	A specific amount of uncured resin and reinforcement are placed into the cavity of a matched mold in the open position. As the mold is closed, the pressure increases, causing the mold to fill and the part to form. This method may be used with prepregs also.
Liquid Composite Molding (LCM)	LCM processes include Resin Transfer Molding (RTM), Structural Reaction Injection Molding (SRIM), and Injection Compression Molding. A fiber preform is placed in the mold cavity and a polymeric resin is injected into the sealed mold. A curing reaction is initiated; the part solidifies and is then removed from the mold. Since LCM has a very high, non-recurring tooling cost, it is best suited for high production volumes to lower the cost.
Vacuum-Assisted RTM	The resin is injected into a mold that contains the reinforcement using pressure that is applied by the atmosphere against an evacuated system.
Resin Film Infusion	The resin film is placed in the bottom of the mold. Heat and pressure are then applied, causing the resin viscosity to decrease and spread through the preform.
Expansion RTM	A material that expands when heated is placed in the preform. The resin is infused and the mold is heated, causing the core material to expand and subsequently forcing the resin into the remaining parts of the preform.
Transfer Molding	Similar to compression molding, but the mold is closed when the resin material is injected.
Filament Winding	Fiber spools are mounted to a creel; the strands from each spool are combined and pulled through a resin bath. The strands are then fully activated with an initiator or hardener and the excess resin is removed. Lastly, they are sent through a drying device and wound onto a mandrel, forming the desired part. Filament winding is used more extensively to manufacture composites than all other lay-up methods combined.
Fiber Placement	Similar to filament winding, but enables all axes of motion.
Pultrusion	Continuous fibers are drawn from reels, formed into a general shape, and drawn through a resin bath. The wetted fibers are then shaped as they converge toward a heated die, where curing occurs. Upon die exit, the formed part enters a pulling system, which provides the force that pulls the materials through the entire system. The pultruded part is then cut and trimmed to the desired size.
Thermoforming	Utilizes matrices that can repeatedly be softened or melted on heating and hardened or solidified on cooling, and that can provide increased fracture toughness and higher hot-wet use temperatures (thermoplastics).

PMC MANUFACTURING DEFECTS

Microcracks

Thermal stresses are created during heating and cooling operations since the matrix and reinforcements expand and contract at different rates. This behavior results from differing coefficients of thermal expansion (CTE). Often, the matrix has a greater CTE than do the fibers.[10]

When thermoplastic PMCs are cooled to their service temperature following molding, a volumetric shrinkage of the matrix occurs, exceeding that of the reinforcements. These unequal contraction rates lead to the formation of residual stresses in the fibers and surrounding matrix.[9] When the magnitude of these stresses exceeds the yield strength of the composite, interface debonding may occur, followed by the formation of microcracks (transverse cracks).[2, 6, 9, 11] Curing, on the other hand, leads to the formation of stresses within thermoset PMCs. These stresses increase with increasing temperature, leading to the formation of microcracks.

As the stresses increase, the microcracks gain width and form intricate, meandering patterns within the matrix. This propagation causes the microcrack density to rise, increasing the likelihood of delamination.[5] Delaminations that form as a result of microcracking typically occur where the microcracks meet ply interfaces, an area of increased stress concentration.[10, 12] Microcracks may also form at the leading point of a main crack, absorbing excess energy and preventing the propagation of a main crack.[1]

Experimentation has shown that unless multiple microcracks are present and a critical microcrack density has been reached, delaminations will not occur. Therefore, in practice, microcracks are often assumed to be tolerable at low densities. Nevertheless, it is critical to consider delaminations that could be induced by neighboring microcracks.[11]

Likewise, it can be a detrimental decision to ignore microcracking, as they are often the gateway to further and more disadvantageous forms of damage that lead to changes in a PMC's mechanical properties, such as reduced longitudinal stiffness and thermal expansion coefficients.[12] When a PMC containing microcracks is placed under cyclic or fatigue loading, the risk of failure increases greatly.[6]

Cracks

Cracks are generally characterized by an actual separation of the material. They are visible on opposite surfaces, extending through the thickness. Cracks propagate when the local energy is greater than that which can be absorbed.[1, 2]

Cracking is a processing defect commonly found in the gel coat of a PMC. The gel coat is a protective layer that is applied to the mold prior to reinforcement placement. Although this coat contributes minimally to the structural capability of the part, it does protect the parts. As a result, it must be able to withstand large stresses, especially during molding and demolding.[1] Demolding operations add stresses to PMC parts, especially when parts stick to their mold and require alternate methods of removal.†† When these stresses exceed the material strength, cracking occurs. To prevent sticking, gel coats are often treated with release agents which, if prepared properly, should have minimal sticking.[1]

When placed in use, structures and parts experience added stresses that can contribute to cracking as well. These stresses couple with already-present manufacturing stresses, insufficient to initiate cracks alone, and lead to the formation of cracks. Under loading, stress concentrations may be created at the intersections of matrix cracks and reinforcements.[2] The added stresses cause the cracks to travel along the edge or surface of the reinforcement, where it must break interface bonds between the reinforcement and matrix. Eventually, the load is transferred completely from the matrix to the reinforcement, which absorbs excess energy through elongation. This energy is dissipated through the formation of internal atomic cracks.[1] As stresses intensify, delaminations may occur, leading to a rapid decay in stiffness and strength and, eventually, catastrophic failure.[2]

Moisture Absorption

Composites absorb moisture through the matrix, fiber, fiber-matrix interface, porous regions, and areas where microcracking and delamination have occurred. Although matrix materials typically absorb more moisture than the reinforcements, the reinforcements do aid in moisture absorption. Water and other liquids often travel via capillary action along the reinforcement until it is absorbed by the matrix.[1]

Moisture absorption is unfavorable since it chemically alters liquid resins, lowering the glass transition temperature‡‡ and degrading mechanical properties, such as elasticity and strength. The reinforcements often act as barriers against moisture diffusion, creating additional stresses within the matrix material. Thus, moisture absorption can lead to swelling due to the restrictions. If allowed to freeze, a separation between the matrix and reinforcing materials or between the layers in a laminate can occur, leading to delaminations.[2]

To prevent moisture absorption, susceptible materials should be stored in low humidity environments. Moisture should be removed from thermoset PMCs prior to high temperature cure to prevent expansion and subsequent delamination.[2]

Temperature Effects

Changes in temperature contribute greatly to the stresses and strains experienced by PMCs. In laminates, heat can cause a free expansion of the laminate layers. If this expansion is restricted by the adjacent laminate layers due to differences in reinforcement direction, internal stresses and failure may result.[2]

At temperatures above the glass transition temperature, thermoplastic matrices can soften to a point at which they no longer efficiently transfer loads, leading to premature failure.[2, 5]

Voids/Pores§§

Voids form from the entrapment of volatile gasses, air, or non-solid foreign materials, and they are virtually incapable of transmitting structural stresses or non-radiative energy fields.[2, 12, 13]

Voids result from dissolved and absorbed water and gases on the prepreg; residual volatiles (i.e., solvents) in the resin and condensates that form during cure; the entrapment of gases during resin mixing operations; or as a result of ply bridging and wrinkling. They can also be produced from the use of improper pressure during the cure cycle, inadequate use of adhesives in bonded structures, and the improper fit of adjacent surfaces.[2] Pores often arise from inadequate wetting of the fiber by the resin or from the inadequate infiltration of fiber tows.[14]

Voids greatly affect several matrix-dominated properties including interlaminar, compressive, and transverse tensile strengths. Interlaminar strength can be reduced by nearly 7% for every 1% of voids present, up to a void content of 4%.[14] Additionally, for each 1% increase in voids, the fatigue life of a fiber-reinforced PMC is reduced by 50% and the strength by approximately 5%. These reductions in strength properties lead PMCs to be more susceptible to degradation in aggressive environments.[13] The accepted void limit in practice is between 2 and 2.5%.[2, 12]

Voids can be eliminated from the final PMC product by drying prepregs in humidity-controlled rooms prior to lamination. Pores, on the other hand, should be removed during the autoclave process since they are nearly impossible to remove from the prepreg.[13]

Inclusions

The encapsulation of solid, foreign materials often leads to physical and mechanical discontinuities within a material. Material inclusions occur most often in uncured thermoset composites that are susceptible to environmental contamination from a variety of sources, including oil, grease, and silicone-based products. Compressed air and the careless application of release agents are common sources of contamination.[2]

Although inclusions are often capable of transmitting structural stresses and energy fields, the transmission rate is noticeably different from that of the parent material. This results in internal stresses that can lead to failure.[2]

Table 3 provides a summary of the common PMC manufacturing defects discussed in this article as well as others that were not discussed.

Delamination, one of the most commonly observed failure modes in composite materials, is characterized by the separation of the fiber and matrix at their interface. Although caused by increasing stress concentrations within a composite, poor process control, poor dimensional tolerance, faulty hole-drilling procedures, and inclusions of the release film during fabrication all contribute to delaminations. Failures often occur near free edges (the region where the load is transferred from the fibers to a weak matrix), around holes at the end of bonded components, or from impact that causes separation of the components.[2]

Table 3. Summary of process-induced defects commonly encountered in PMCs.[15]

Contamination	Due to foreign particles, extraneous fibers, or pieces of plastic release film (peel ply) not being removed from prepreg surface, etc.
Undercure or Variation in Degree of Cure	Occurs if the proper temperature and/or time are not used during the cure process
Delamination or Separation of Plies within the Laminate	Due to poor consolidation and undercure in the curing operation or created during hole drilling or machining of a cured composite
Voids	Formed by entrapped air, the presence of moisture, an excessive amount of solvent, or the release of gases during the curing reaction
Resin-rich or Fiber-starved Areas	Caused by nonuniform resin distribution or flow during molding
Resin-starved Areas	Caused by an uncontrolled, or lack of, resin flow through the reinforcing layers
Fiber Misalignment	Due to misoriented fibers, deviation from the preselected layup or filament winding pattern, or fiber washout from excessive resin flow
Broken Filaments	Caused by scratches or cuts, or a drill during hole drilling processes
Fiber Waviness or Kinking	Due to improper tensioning during prepreg preparation, filament winding, and pultrusion

SUMMARY

An understanding of the basic PMC material defects, which result from manufacture, is crucial for the prevention of property degradation and catastrophic failure. This article surveyed several of the common manufacturing-induced PMC materials defects.

NOTES & REFERENCES

* Polymeric materials are composed of several small repeating units known as monomers.

† Plastics are polymeric materials (usually organic) of large molecular weight that can be shaped by flow; the term plastic usually refers to the final product with fillers, plasticizers, pigments, and stabilizers included. Often, this term connotes thermoplastics.

‡ Resins are any class of solid or semi-solid organic products of natural or synthetic origin with no definite melting point. Resins generally have high molecular weights; most resins are polymers. The use of the term resin connotes a thermoset composite material.

§ The debulking process reduces the void content by removing the excess air contained within the composite. This process typically follows lay-up operations.

** Prepreg is shorthand for pre-impregnated material. A prepreg is a ready-to-mold material that is impregnated with a resin. The resin is usually partially cured to the B-stage and supplied to the fabricator, where it is formed into the desired shape and cured completely.[3]

†† In industry, stuck parts are typically discarded as a result of the damage incurred during removal.

‡‡ The glass transition temperature is the temperature at which the matrix changes from a glassy state to a viscous state.

§§ The terms void and pore are oftentimes used interchangeably. For the purposes of this article, voids refer to the empty spaces beneath the surface of a PMC. The empty spaces on the surface of the PMC are termed pores.

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