High Barrier Carrier Release Films For Thermoset Reinforced Plastics

By Paul Jackson, PolyGroup Inc.

Introduction to Thermoset Fiber Reinforced Plastic Composites

Thermoset fiber reinforced plastic (FRP) compounds are formulated to exhibit tight dimensional control, toughness, high strength to weight ratio, design flexibility, creep resistance, heat/flame resistance, high dielectric strength, chemical resistance, corrosion and stain resistance, long-term durability and color stability. Many of these properties may be customized for specific end-use application requirements. ***High barrier carrier release films*** and their usefulness are explained after an overview of applications, materials and processes for both Sheet Molding Compounding (SMC) and Bulk Molding Compounding (BMC).

Applications

Thermoset reinforced plastic composites are safe and reliable solutions, able to face tough conditions in various environments and have outperformed traditional materials for many years. Fiber reinforced thermoset materials are excellent candidates for products being considered as metal replacement.

Typical applications for these materials are electrical enclosures, circuit breakers, toggle bars, levers, switch bases, low voltage insulators, under the hood automotive caps and housings, seats, shower and bath fixtures, small and large appliance handles, control panels, side and end panels, serving trays, microwave safe cooking trays, outdoor grill shelves and control knobs, lighting luminaires, bases and cover, entry door skins and many others.

Materials

Unsaturated Polyester

It is estimated that approximately 75 percent of all the resins used in thermoset FRP composites are produced from unsaturated polyesters. Unsaturated polyesters are copolyesters prepared from a dicarboxylic acid such as unsaturated phthalic anhydride or saturated maleic anhydride. These two acid constituents are reacted with one or more dialcohols, such as ethylene glycol or propylene glycol, to produce the characteristic ester groups that link the precursor molecules together into long, chainlike, multiple-unit polyester molecules.

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Reinforcements

Fibrous reinforcements are added to the unsaturated polyester to increase the impact strength of the end product. The most common reinforcement is fiber-glass because it is cost effective and creates a cured end product with high impact strength. Fiberglass has a long historical record of proven performance in FRP applications. Carbon fiber reinforcement plastic (CFRP) is rapidly growing for specialty applications as a result of its inherent strength to weight ratio and opportunity for producing light weight parts. However, the high cost of carbon fiber materials and slow manufacturing throughput are currently tough challenges for implementation in the broader market. Reinforcement content is generally concentrated between 15 and 60 percent by weight of the composite mixture and typically chopped into strands between 1/8" to 2" lengths depending upon the type of process and desired properties. Continuous fiber roving may be chopped in process or be purchased in chopped form depending upon the material, process technique and equipment capabilities.

Fillers

Inorganic fillers, usually 30 percent to 70 percent of the mixture by weight, are used to further enhance the performance of the end product. The two most common fillers are calcium carbonate and kaolin clay. The addition of fillers reduces the amount of fiber reinforcement needed, improves flame retardance and lowers the cost. Fillers can also enhance physical properties and help control viscosity of the polymer mixture for better processing, handling and cutting prior to molding.

Additives and Modifiers

Between one percent and five percent of the weight of the unsaturated polyester mixture consists of additives and modifiers. Additives can include initiators to control polymer gel time (tert-butyl benzenecarboperoxoate), mold release agents (zinc stearate and calcium stearate), pigments (titanium dioxide, carbon black, iron oxides, etc.), thickeners (magnesium oxide, calcium carbonate, magnesium hydroxide, and calcium hydroxide) tougheners (copolymer conjugated dienes, elastomers, rubber), stabilizers, flame retardants, and low profile

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additives for surface enhancement and shrink control such as Fipolder™ FHP05080 fine polyethylene fine powder manufactured by Two H Chem Ltd. and distributed by PolyGroup Inc., Cincinnati, OH.

Crosslinking Agent

The thermosetting resin is produced by dissolving low-molecular-weight unsaturated polyester in a reactive vinyl monomer, which is typically styrene, to lower the viscosity of the product. This decrease in viscosity also makes the polyester easier to handle and process. After other components are added (reinforcements, fillers, additives and modifiers), the mixture must not be allowed to cure until formed into the final functional part. Final forming occurs when the mixture is heated during molding, causing the vinyl monomer to fully react with the polyester. The heat and compression induced reaction changes the mixture by crosslinking or curing the polymer components to a hard and durable thermoset material.

Processes for Thermoset Fiber Reinforced Plastics

Sheet Molding Compounding (SMC) and Bilk Molding Compounding (BMC) processes are commonly utilized in the manufacture of thermoset fiber reinforced plastic composites. SMC and BMC are similar in material composition but different in form and process. Both processes commonly begin with mixing (screw mixer, sigma blade mixer, or plough blade mixer) of similar components into a “pre-mix” and are molded into a final part using heat and compression. However, there are many differences in formulation, sequence of operation and form of the compounding before molding into the final part.

Sheet Molding Compound (SMC)

Sheet molding compound is a ready to mold flat laminate of thermosetting resins and fiber reinforcements. Sheet molding compounds are suitable for compression molding a wide range of part sizes from simple panels to complex shapes.

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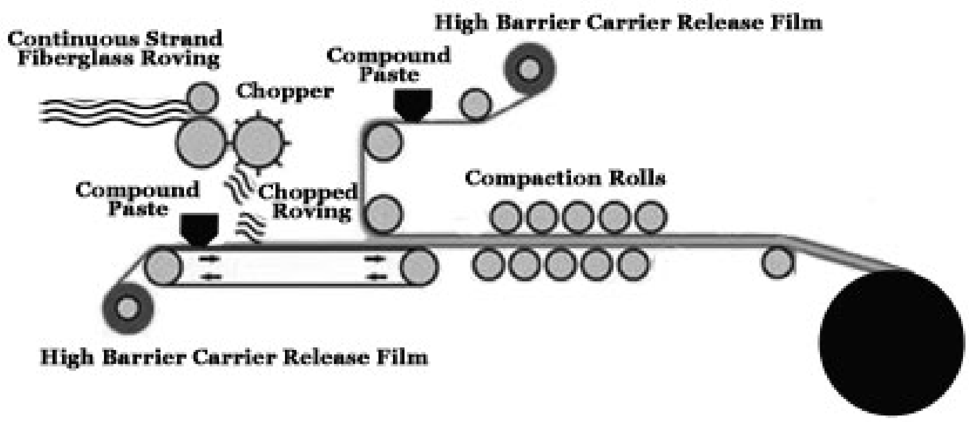
Manufacturing of SMC is a continuous in-line process. The base components are bulk mixed into a paste and continuously metered onto to the surface of a ***high barrier carrier release film*** that acts as a substrate. A doctor blade system ensures even distribution of resin paste across the entire substrate prior to the introduction of fiberglass to the product. Once the fiberglass or carbon fiber is laid, a second coating of compound paste is deposited onto a second top layer of ***high barrier carrier release film*** and combined to make a three layer sandwich like structure. The top and bottom ***high barrier carrier release films***, paste & reinforcement fiber are then brought together in the compaction section, where the layers are compressed with belts and/or rollers into one multi-layered sheet.



SMC Manufacturing Process

The sheet is then rolled on a core or fan folded into a container and stored in a controlled environment where maturation to a specified viscosity takes place. The resulting pliable sheet is flexible enough for handling and rigid enough for cutting.

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Sheet Molding Compound with High Barrier Carrier Release Films

The ***high barrier carrier release films*** are removed from the top and bottom of the sheet compound prior to molding. The sheet compound is then placed between matched dies that are compressed and cured to a state of high level cross linking using a specified set of time, temperature and pressure conditions.

Bulk Molding Compound (BMC)

Bulk molding compound is a ready to mold pre-peg of thermosetting resins and fiber reinforcements. A pre-preg is a semi-finished thermoset compound not yet cured. Pre-peg commonly comes in the form of bulk for injection molding or extruded and precisely weighed compound in preparation for compression molding. Injection molding of BMC is used to produce components with more complex shape and high volume industrial applications.

Like SMC, BMC is a mixture of polymer resin, inert fillers, fiber reinforcement, catalysts, pigments, stabilizers, release agents, thickeners and low profile additives that that are formed into a viscous compound for molding. BMC generally contains less fiber reinforcement with shorter fiber lengths typically between 1/8" and 1/2" in length compared to SMC. The chopped fiber strands may further vary in length depending on the level of performance required. Reinforcement content generally ranges between 15 and 20 percent; however, it may

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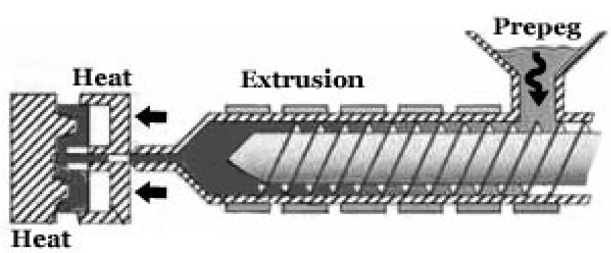
reach 25 percent or higher. BMC uses lower reinforcement content than SMC and permits higher filler loadings for lower cost.

Filler content and thickeners can also differ from SMC in order to provide improved flow characteristics that impart a high level of detail and dimensionally precise parts. Mixing equipment and sequence of operation for adding components during compounding can also differ compared to SMC. The process equipment chosen is dependent upon specific product properties, product form and volume. Preventing fiber breakage is a key concern when mixing BMC compound.

Unlike SMC, it is not necessary to include a maturation stage if directed immediately to an injection molding machine for molding. For injection molding, the compound pre-peg is loaded into a hopper with a stuffer, fed to the extruder and injected into a heated precision mold. BMC injection extruders have a non-return valve for the thermoset materials. The parts are released hot after complete curing of the thermoset.



BMC Injection Molding Process

BMC – Injection Molding Pre-peg

For compression molding, BMC compound is typically extruded into a cylinder shape and precisely divided into a predetermined weight and/or volume to suit the molded part requirement. This precisely divided compound is most often referred to as a pre-peg charge or dough charge. The pre-peg charge is then packaged into an individual bag or bulk bag created from ***high barrier carrier release film*** to slow curing for compression molding at a later time and/or location. The pre-peg charge is removed from its ***high barrier bag*** and placed be-

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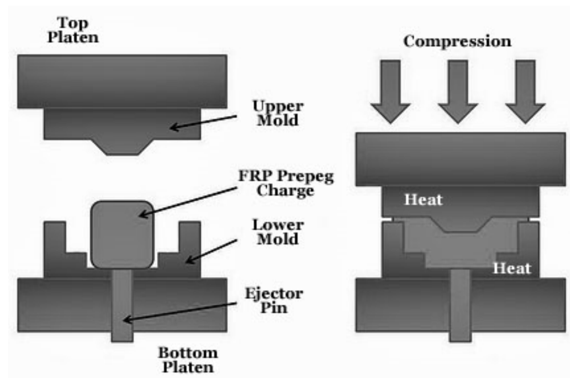
tween matched dies that are compressed and cured to a state of high level cross linking for a specified set of time, temperature and pressure conditions.

BMC – Pre-peg Charge in High Barrier Bag



BMC Compression Molding

After complete cure the parts are released hot. The process produces a high quality surface manufactured with short cycle times.

High Barrier Carrier Release Films in SMC/BMC Processes

High barrier carrier release film is a necessary and highly valued contributor in SMC and BMC manufacturing processes. The film is most commonly produced using the blown film process as a result of its high speed production, accurate multiple layer control, capability for producing thin plastic films and its relative low cost to manufacture compared to the cast film process.

Key Film Characteristics

High Barrier to Volatiles and Chemicals

The term “high barrier” with regard to SMC/BMC applications is defined as the prevention or significant reduction in the migration of styrene monomer and other volatile liquid aromatic hydrocarbons through a plastic protective film.

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The primary purpose of ***high barrier carrier release film*** in thermoset polyester SMC and BMC compounds is to slow the release of styrene monomer volatiles that would otherwise induce an excessive increase in viscosity and/or premature cross-linking prior to molding. Controlled atmosphere warehousing is also often used to slow curing and control excessive viscosity increase by maintaining a moderately cool constant temperature during storage. The combination of ***high barrier carrier release film*** and temperature controlled cold storage prior to molding slows curing of SMC and BMC compounds to provides better product consistency, more predictable molding characteristics especially during seasonal environmental changes and prolonged shelf life.

There are many possible solutions for providing a flexible film barrier to volatile and chemical migration. Options may include aluminum foil, ethylene vinyl alcohol copolymers (EVOH), several types of polyamides and copolymers, Polyvinylidene chloride (PVdC), polychlorotrifluoroethylene (PCTFE), silicon or aluminum oxide based thin film coatings deposited onto polyethylene terepthlate (PET) and oriented polypropylene (OPP) metal oxides by plasma-deposition, and others.

However, few can offer the combination of properties that include ease of manufacture, market availability, low cost, production flexibility, excellent physical properties, thermal stability, chemical resistance and high barrier to volatiles offered by polyamides (Nylon).

Low Surface Tension

The ***high barrier carrier release film*** applied to the top and bottom surfaces of the compound must then be stripped off with easy “release” from the unsaturated polyester compound prior to the compression molding step.

A monolayer polyamide polymeric film provides good barrier characteristics for the styrene monomer but is largely unsuitable for use because the Nylon tends to adhere to the styrene monomer containing compound. Nylons adherence to the compound makes it difficult to remove prior to molding.

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Solving the problem of Nylon adherence requires another polymer that provides a non-polar low surface tension contact layer that is largely unaffected by styrene monomer and other highly volatile liquid aromatic hydrocarbons, such as low levels of benzene and toluene that may be employed in the SMC/BMC compound. Polyethylene is an ideal selection for its non-polar and non-adherence to unsaturated polyester compound formulations. In addition, it has the advantage of being a relatively low cost commodity resin widely available in in the marketplace. By comparison, Nylon engineering materials are roughly estimated to double the cost of polyethylene depending on market price swings. Polyethylene alone would be exceptionally permeable to common volatile liquid aromatic hydrocarbons making it unsuitable to be used without a Nylon barrier layer.

Multiple Layer Film

The layered combination of polyethylene on the outside contact layers of the unsaturated polyester compound and Nylon in the core layer was created in a coextruded blown film to provide the balance of properties suitable for SMC/BMC applications.

The most versatile and common coextruded multiple layer film suitable for SMC and BMC is a five layer film structure consisting of polyethylene/ adhesive/ Nylon/ adhesive/ polyethylene such as those ***high barrier carrier release films*** manufactured by General Films Inc., Covington, OH and distributed by PolyGroup Inc., Cincinnati, OH. The film manufacturer often tailors this basic coextruded film structure to suit customer and/or application preferences. Polyethylene layers may be made from high density polyethylene, low density polyethylene, liner low density polyethylene (butane, hexane or octane comonomers), very high comonomer content plastomers, polypropylene, ethylene vinyl acetate copolymers and many others including blends therefrom to achieve desirable performance characteristics. A polymer adhesive component is required to provide high bond strength between the polyethylene and Nylon materials. These extrudable grade adhesives are commonly polyethylene based materials with added functional groups such as maleic anhydride to acquire the necessary bond strength. Finally the inside polyamide core layer of the coextruded film is selected for its barrier to styrene monomer and other volatile liquid aromatic hydrocarbons. The most preferable polyamide is Nylon 6/66, which is a copolyamide of hexamethylene diamine, adipic acid, and caprolactam. Nylon 6/66 copolymer provides superior flexibility and crack resistance, lower melting point and ease of manufacture making it the most often preferred barrier material of choice for SMC and BMC ***high barrier carrier release film***. Nylon 6 melts at 250 °C (482°F) and Nylon 6/66 has a melting point of 200 °C (392°F).

Film Heat Seal Properties

As previously described herein, the ***high barrier carrier release film*** is layered on the top and bottom of the SMC compound paste and combined to act as a barrier to prevent styrene monomer and other volatile liquid aromatic hydrocarbons from migrating out of the compound. Undue loss of styrene may still escape from the edges of the film. When styrene volatiles escape through the edges of the SMC, the sheet becomes styrene deprived causing unwanted crosslinking to occur rendering the edges of the sheet as costly waste. Therefore, sealing the edges of the film to prevent volatiles from escaping is often employed during the manufacturing process. Sealing of edges ensures consistent maturation across the entire width of the sheet.

However, a locking heat seal, or one that cannot be separated without cutting or tearing it open is most often not desirable. Locking heat seals often require costly and troublesome film edge cutting equipment. In order to eliminate production inefficiencies and capital cost, a peelable heat seal is employed. A peelable heat seal is one that seals to prevent migration of styrene monomer and other volatile liquid aromatic hydrocarbons but allows for low force separation. The manufacturer of ***high barrier carrier release films*** use proprietary materials and additives to achieve controlled peal forces. These peel forces vary but are often found to be between 0.5 to 2.0 lbs. of separation force. Once top and bottom ***high barrier carrier release films*** are separated prior to molding, the high film can be gathered for disposal and/or sent to a recycle stream.

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BMC with precisely weighed pre-peg may also utilize a heat seal on individual ***high barrier release carrier bags or bulk bags*** but are often simply folded and or twisted close to slow the migration of styrene monomer and other volatile liquid aromatic hydrocarbons.

Mechanical Strength and Toughness

The SMC process is physically demanding of ***high barrier carrier release film*** during manufacture. It must support the weight of the unsaturated compound by resisting elongation, abrasion, tearing and breakage as it is "carried" or moved along through the system of mechanical conveyors, rollers and windings. Top and bottom films are generally of the same construction and formulation for logistical efficiency. Therefore, ***high barrier carrier release films*** are most commonly designed for the most demanding property requirements regardless of usage on top or bottom of the sheet molding compound.

The user of ***high barrier carrier release film*** would like to achieve the aforementioned mechanical properties at the lowest possible cost and efficiency. Since ***high barrier carrier release films*** are utilized as a covering for SMC compound, they are preferably priced as cost per unit of surface area ($/inch2) which removes consideration for weight and/or density. Therefore, a user has the economic objective to produce the thinnest gage possible while maintaining critical performance characteristics. Over many years of film development and processing history in SMC production facilities, it has been established that a PE/Adh/Nylon/Adh/PE coextruded film structure provides adequate barrier to volatiles permeation and offers the required mechanical performance with an average thickness generally between 0.9-1.5 mil (1 mil=0.001 inch). Nylon 6 or Nylon 6/66 makes up only 20-40% of the multi-layer film structure but provides the primary tensile strength and resistance to longitudinal and horizontal elongation. Polyethylene and/or blends made primarily of polyethylene with other polymers makes up 60-80% of the film structure and is the primary contributor to tear resistance and low surface tension release from the FRP compound. The multi-layered coextruded blown film made from the combination of Nylon

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and polyethylene provides mechanical strength, toughness and economic benefit that neither material could provide alone.

Color and Visibility

It is highly desirable to add a visible coloring agent to ***high barrier carrier release film***. Color provides greater visibility of the ***high barrier release carrier film*** during use. Generally, a bright color pigment, such as orange, red, blue or yellow, is incorporated into the polyethylene layer composition. The purpose of brightly colored film is to alert the manufacturer that film is present on the SMC compound surface. If the **high barrier release carrier film** were to tear, the brightly color would stand out from the background color of the SMC alerting the technician to any film pieces remaining on the surface. It is equally important to minimize pigment loading to ensure high translucency and good contact clarity to visually inspect the quality of the SMC during manufacture. Contact clarity for BMC ***high barrier release carrier film*** is also of great importance due to the use of infrared sensors to control applied paste quality and real-time processing adjustments.

BMC precisely weighed pre-pegs may also utilize color pigment on individual ***high barrier release carrier bags or bulk bags*** but most often exhibit the naturally clear translucency of the polymers made therefrom.

Contaminate Protection

High barrier release carrier film prevents dust, dirt and other contaminates from sticking to the surface during manufacture, storage and transport.

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Summary

The information provided herein provides basic understanding applications, materials and processes for thermoset reinforced plastics. There are many more details and variations in product formulation, equipment and process techniques for further reading. Developments in SMC and BMC continue to be driven in part by improved performance, light weighting, and manufacturing efficiency through faster cycle times and lower materials costs. ***High barrier carrier release film*** is a necessary and highly valued contributor in SMC and BMC manufacturing processes. Today's most widely accepted coextruded multiple layer film consisting of polyethylene /adhesive /Nylon /adhesive/ polyethylene provides the barrier to volatiles migration and physical performance required for SMC and BMC compounds. Many variations of ***high barrier release carrier film*** are possible to accommodate the needs of the user, products and process differences. The film producer has many tools to modify films using additives, a vast selection of polymer types, coextrusion layer construction, and processing techniques to meet the demands of the thermoset reinforced polymer manufacturer.

PolyGroup Inc. was formed in 2003 in the greater Cincinnati, Ohio area and is an innovator and marketer of specialty thermoplastic polymer products to industry processors, formulators and converters. PolyGroup Inc. products are differentiated from commodity plastics by their unique properties and/or function. PolyGroup Inc. represents and distributes for Two H Chem Ltd. and General Films Inc. TWO H Chem Ltd. specializes in the production of customized polymer products including thermoplastic powders, adhesive resins, films and specialty compounds. General Films Inc. specializes in the production of customized coextruded blown films for food, beverage and non-food packaging application. Visit our website at www.PolyGroupInc.com.

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