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DEVELOPMENTS IN HIGH BARRIER NON-FOIL PACKAGING STRUCTURES FOR MILITARY RATIONS

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Abstract

Technologies directed at developing high barrier non-foil packaging structures are being explored for potential use in military ration packaging, such as the Meal, Ready-to-Eat (MRE). Foil is currently used as the barrier layer, due to stringent oxygen and water vapor barrier required to meet the three-year shelf life. Performance, manufacturing and waste issues associated with the current packaging structure have created a need for non-foil packaging. This investigation focuses on several key technologies such as recyclable and biodegradable polymer nanocomposites, layer multiplying technology, barrier coatings, encapsulated PVDC co-extrusion, and chaotic advection.

Background

The Army initiated a move toward an alternative (non-cans) combat ration in the late 1940's when it was proposed that food could be heat processed in flexible packaging materials.[1] The Meal, Ready-to-Eat (MRE) is used by the Services to sustain individuals during operations that preclude use of organized food service facilities, but where re-supply is established or planned.[2] The MRE, shown in Figure 1, was developed in response to changing operational and organizational concepts, and was adopted as the DOD combat ration in 1975.

Figure 1. MRE Components

The range of environments in which the MRE is utilized spans the globe. For this reason, MRE packaging must maintain its properties in humid or dry conditions, as well as at temperatures ranging from arctic to desert or tropical. The minimum shelf life requirement for the MRE is three years at 80 ^{o}F, and six months at 100 ^{o}F. To meet these stringent shelf life requirements, the specified oxygen and water vapor transmission rates for the MRE retort pouch are 0.06 cc/m^2/day, and 0.01 g/m^2/day, respectively. The packaging must provide protection from microbiological contamination, as well as insect and rodent penetration and infestation. The MRE must also be capable of withstanding various levels of abuse during transportation and distribution, including low altitude freefall airdrop of individual cases and high altitude parachute drop of pallet loads.[1]

There are several monolayer and multilayer film structures currently used in MRE packaging. The four major packaging components include a retort pouch, non-retort pouch, over wrap for commercial items, and a Meal Bag. The retort pouch is a quad laminate structure with the following sequence from the outer to inner layer: polyester, polyamide, aluminum foil, polyolefin. In some structures the sequence of polyamide and aluminum foil may be reversed. The non-retort pouch and over wrap have a structure similar to the retort pouch, with the exception of the nylon layer being absent. The nylon layer is added to the retort pouch for increased durability in cold weather situations, when liquids commonly found in retorted food items can freeze and puncture the foil layer. The main structural difference between the non-retort pouch and over wrap is layer thickness. The Meal Bag, a 10-mil low density polyethylene (LDPE) film, is used to contain the individual components of the MRE, and to prevent insects from penetrating the packaging.

There are several reasons why the Army is exploring high barrier non-foil packaging structures. The inherent properties of foil present a number of limitations in regards to performance and manufacturing. Although foil offers ultimate resistance to gases, vapors, and light blocking, in cold weather and high impact situations, such as airdrop, foil is especially susceptible to pin holes and stress-induced fractures. There are also a number of manufacturing issues encountered with foil based film structures. Incorporation of foil into the center of a structure requires multiple lamination steps. Removal of the foil layer has the potential to minimize the processing steps required to produce a multilayer film. Developments in co-extrusion equipment have the potential to reduce the process to a single step. New technologies focusing on thermal isolation allow polymers with large differences in melting temperature to be processed together on a single coextrusion line, as opposed to extruding separate films and laminating in a second step.[15] Foil also limits pouch forming processes. For example, foil prevents a deep draw of the web during horizontal form fill seal (HFFS). Shallow draws can be a problem during filling, allowing food product to spill onto the sealing area of the web. Foil based structures are also limited to certain food processing techniques. Removal of the foil layer would expand the range of techniques used to sterilize rations. Processes such as microwave, high pressure pasteurization, and radio frequency sterilization are alternative food processing techniques that could potentially improve the quality and acceptability of food. However, they cannot be used with the current foil based structures.

The Army is also investigating non-foil packaging due to the fact that foil-based packaging results in a non-recyclable package, which generates excess waste. The Army, Air Force, and Marine Corps consume approximately 46.6 million operational ration meals per year. Consumption of these rations generates approximately 14,117 tons of packaging waste, amounting to 0.66 lb of packaging waste per warrior per meal.[2,3] Studies focusing on creating a high barrier non-foil packaging structure coincide with the military's waste reduction effort. It is possible to have recyclable MRE packaging by eliminating the foil layer. Although developing a non-foil film structure that meets the militaries stringent barrier and mechanical properties is a challenge. One step further would be to produce a biodegradable film structure, which could be composted or buried in the soil at base camps. However, recyclable and biodegradable ration packaging is only beneficial to the waste reduction effort if the appropriate recycling and compost facilities exist. These efforts are driven by current research in the area of nanocomposites, barrier coatings, and chaotic advection.

Another effort in the area of waste reduction is down gauging. Inner packaging components such as the retort and non-retort pouch have the potential of being down gauged by building barrier properties into the outer Meal Bag. The Meal Bag itself is also a candidate for down gauging, since it is currently 10 mil thick. Replacing the Meal Bag with a thinner, possibly multilayer film, with added barrier would allow for reduction of packaging materials in both outer and inner components.

Due to the large amount of packaging waste associated with rations and the limitations of foil based packaging, a number of programs focusing on waste reduction and high barrier non-foil packaging have been funded by government committee's such as Strategic Environmental Research and Development Program (SERDP) and The Combat Feeding Research and Engineering Board (CFREB). These programs focus on reduction of waste and development of a non-foil high barrier packaging structure.

Non-Foil Packaging Strategies and Research Progress

Nanocomposites

Conventional fillers such as minerals, metals, and fibers have been added to polymers for decades to produce composites with improved mechanical and thermal properties.[4] In the late 1980's, research focusing on nanocomposites, employing nano-fillers, yielded equal if not better property improvements using only a fraction of filler that would normally be required.[4] High-aspect-ratio nano-fillers also provide improvements in barrier performance and clarity without a significant increase in density, which is not feasible with conventional composites.[4]

Nanocomposite studies at Soldier Science Center (SSC) have incorporated montmorillonite, a layered silicate commonly used in polymeric nanocomposite systems. Montmorillonite layered silicates (MLS) have high cation exchange, high surface area (around $750 m^2/g$), and large aspect ratio with a platelet thickness of 10 Å.[5] The closely stacked structure of the silicate layers and chemical incompatibility between the hydrophilic clay and hydrophobic polymer are two significant challenges when developing an exfoliated nanocomposite with improved properties.[6] Organically modifying the MLS by replacing inorganic exchange cations with organic onium ions on the gallery surfaces has been shown to compatibilize the MLS and polymer, and also leads to increased basel spacing between the silicate layers due to the bulky organic ions.[6] Greatest property improvements have been seen in exfoliated systems, where silicate layers have delaminated and are homogeneously dispersed into the polymer matrix.[7] Polymer nanocomposites studied at Natick have been shown to be anywhere

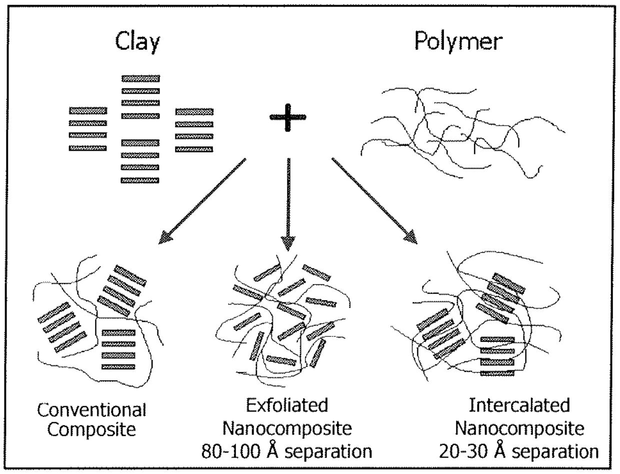

Figure 2. Composite morphologies

from intercalated to highly intercalated. Figure 2 shows morphologies found in conventional and nano-sized composites.

SSC has studied both biodegradable and recyclable polymer nanocomposites for applications in MRE packaging. Biodegradable polymers include polylactic acid (PLA) and polyhydroyalkanoates (PHA). Recyclable polymers include LDPE, ethylene co-vinyl alcohol (EVOH), and polyethylene terephthalate (PET). These polymers were chosen based on their barrier properties and potential use as food packaging.

Studies focusing on EVOH nanocomposites have been initiated to further improve the polymers already exceptional oxygen barrier. Copolymers of ethylene and vinyl alcohol are highly crystalline resins produced with various levels of ethylene content. Oxygen barrier varies according to the ethylene content in the polymer and is adversely affected by the amount of moisture absorbed. However, the loss of oxygen barrier as a result of moisture absorption can be greatly diminished by coextruding EVOH between layers of high moisture barrier resins.

Several formulations of EVOH nanocomposites processed on both cast and blown film extrusion lines have been studied and analyzed. Transmission electron microscopy (TEM) and wide angle x-ray diffraction (WAXS) are used to analyze morphology. Barrier, mechanical and thermal properties are also studied to determine the effect of MLS on EVOH. The WAXS pattern in Figure 3 shows a significant shift to the left for the nanocomposite film with 3% MLS (Closite 25A, Southern Clay Products) loading, indicating interaction between the MLS and polymer. As reported by Dennis et al., an average *d*-spacing between 20–30 Å indicates an intercalated

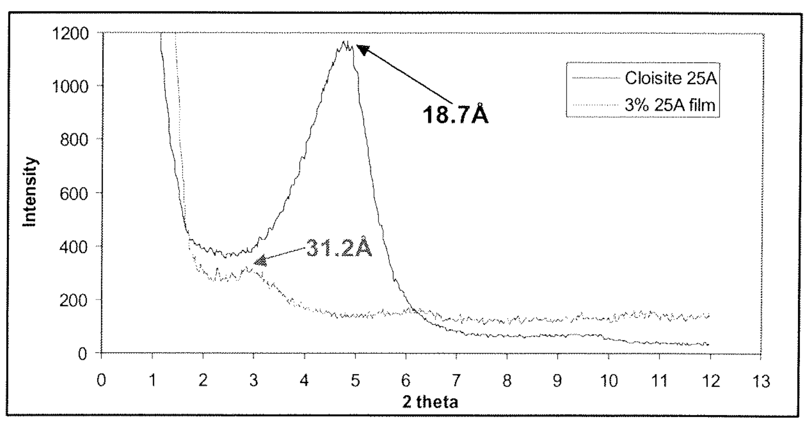

Figure 3. WAXS curves for Closite 25A and E-105 film with 3% 25A loading

system[7]; therefore suggesting that this EVOH/MLS nanocomposite system, with a *d*-spacing of 31.2 Å, is highly intercalated. TEM images confirm the presence of an intercalated nanocomposite film, and also show that blown film processing imparts significant improvement in MLS alignment over the compounded pellet and cast film nanocomposite with identical formulation.[13]

As shown in Figure 4, the Young's modulus of the blown film EVOH nanocomposite with a 3% MLS loading shows improvements over the pure blown film at higher relative humidity levels. At 93% RH the EVOH nanocomposite shows a 58% improvement in Young's modulus over the pure. An identical formulation processed on a cast film extrusion line also shows improvement in Young's modulus, but not to the extent of the blown film. Better orientation during blown film processing may explain the differences observed between these two films.[13]

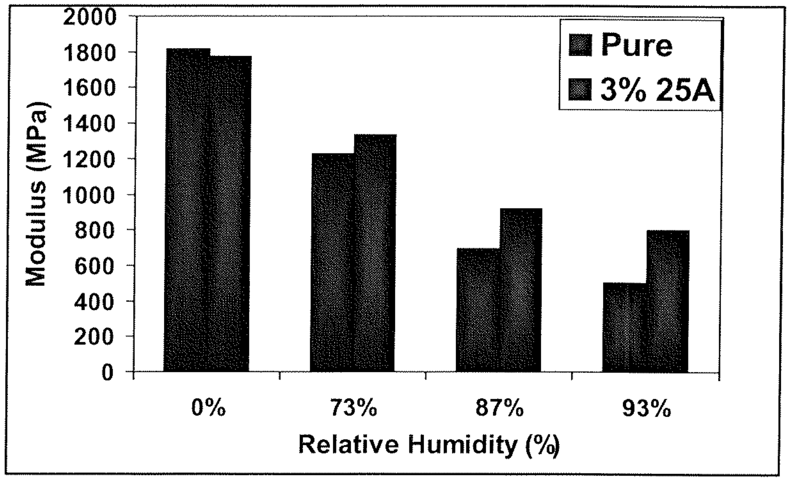

Figure 4. Effect of MLS on Young's modulus of EVOH

Barrier properties were significantly different between cast and blown film nanocomposites. As shown in Figure 5, the cast film EVOH nanocomposite shows a much lower oxygen transmission rate (OTR) than the blown film. The cast film nanocomposite has a 57% increase in oxygen barrier over the control film, whereas the blown film nanocomposite has a 14% loss in oxygen barrier. Given the higher orientation seen in the blown film samples it is expected that permeability would be decreased, due to a more tortuous path. Further research into what affects the permeability of oxygen and water vapor in nanocomposites is needed to develop nanocomposites

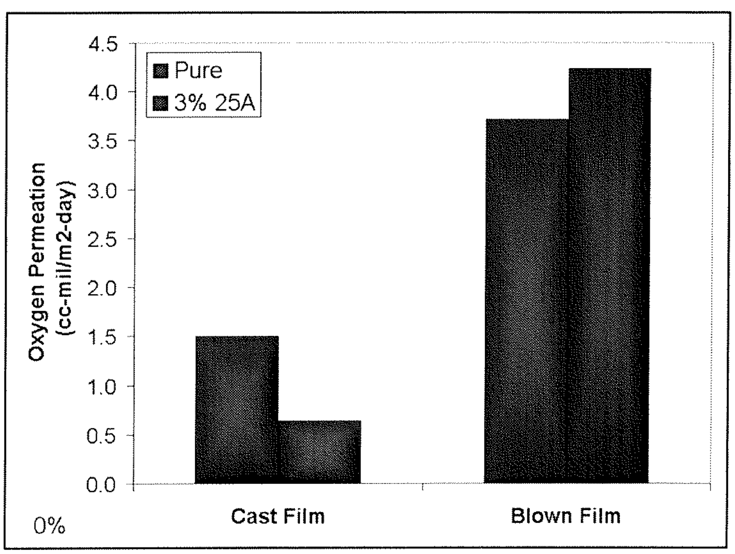

Figure 5. Oxygen transmission rates of cast and blown film EVOH nanocomposites

with maximum property improvement.[13]

LDPE has also shown property improvements with the addition of MLS. The organically modified montmorillonite is combined at low loadings (7.5%) with a compatibilized LDPE and processed as a blown film to give improved thermal, mechanical and barrier properties. TEM of the films at various processing parameters shows that the 7.5% loading has a high degree of intercalation and dispersion. The Young's modulus improved by 80% for the 7.5% montmorillonite nanocomposite in comparison to the pure LDPE. The oxygen barrier improved also, having almost twice the barrier of the pure LDPE, at dry conditions. A pilot size scale-up of the 7.5% montmorillonite nanocomposite was conducted. The transition from laboratory to pilot scale was successful with equivalent improvement of properties. The target application for this nanocomposite system is for the MRE Meal Bag.[14]

Pliant Corporation is also looking into nanocomposites under a DOD/SSC contract entitled "High Barrier Non Foil Packaging Structures for Extended Shelf Life". Pliant will be exploring both commercially available and developmental nanocomposites. Successful nanocomposite formulations identified through this research will be applied to a novel die and layer multiplier technology. This technology uses conventional coextrusion equipment to produce cast and blown films with up to 14-layers incorporating four to five different materials. This system is believed to further restrict the oxygen diffusion rate through the structure. Results are not yet available as Pliant is in the process of designing the layer multiplayer.[9]

Barrier Coatings

Deposition of thin coatings on polymeric substrates is another area of interest in the development of high barrier non-foil structures. Barrier coating technologies allow for the deposition of thin film coatings on polymeric substrates using state-of-the-art processes, and can produce high quality coatings using continuous in-line production techniques. SSC is currently investigating a range of commercially available and developmental coating technologies through the industrial partners listed in Table 1.

Transparent SiOx coated polyvinyl alcohol (PVOH) and PET film samples were obtained from Mitsubishi Plastics, Inc. PVOH based samples showed exceptional barrier to

Table 1. Coating technologies and representative industrial partners

Coating	Substrate	Trade Name	Coater	Converter
SiOx	PET, PVOH	TechBarrier	Mitsubishi Plastics, Inc.	-
AlOx	PET		Toppan Printing Company	Pliant Corporation
SiOx	PET, PP		Dow Corning Plasma Solutions	Appleton

oxygen and water vapor. Samples were tested on MOCON Oxtran 2/21 and Permatran 3/33, in accordance with ASTM D-3985 and F-1249, respectively. Oxygen permeability testing was conducted at 23°C and 100% oxygen concentration, and at both 0% and 90%

RH. Water vapor permeability was done at 37.8 °C and 90% RH. Results show an OTR of 0.013 cc/m^2/day at 0% RH, and a water vapor transmission rate (WVTR) of 0.050 g/m^2/day. These values coincide with reported values, but test conditions for literature values are not listed. PVOH is considered a water soluble polymer, however the PVOH layer in this structure is sandwiched between other materials to protect it from moisture. Oxygen permeability testing at 90% RH resulted in and OTR of 0.052 cc/m^2/day, which is still below the MRE retort pouch specification of 0.06 cc/m^2/day. Partnerships with Pliant and Appleton are the beginning stages; therefore results pertaining to Toppan and Dow Corning coatings are not yet available.

Encapsulated PVDC

Polyvinylidene chloride (PVDC) resins are copolymers of greater than 50% vinylidene chloride and other monomers such as vinyl chloride and methyl methacrylate. PVDC offers exceptional barrier resistance to oxygen and carbon dioxide. Unlike nylon and EVOH, PVDC's oxygen barrier is unaffected by moisture, including high humidity conditions. The permeability of PVDC decreases with increasing mole fraction of vinylidene chloride, due to increasing crystallinity. Conversely, its toughness, flexibility at low temperatures, and heat sealing properties improve with decreasing mole fraction of vinylidene chloride.[8] Recent developments in PVDC have resulted in barrier improvements of 40% over conventional commercially available PVDC resins and films.[9] Resistance to moisture and improved oxygen barrier make PVDC a great candidate for retortable, non-foil packaging applications. The main drawback to this material is that specialized processing methods and/or equipment are required, due to stability issues and retard degradation commonly encountered when processing on conventional extrusion equipment. A novel way of processing this new class of material is by encapsulating the PVDC in a second polymer to protect downstream equipment, and employing precise temperature control to avoid degrading the PVDC.

Pliant Corporation is investigating encapsulated PVDC coextrusion under a Department of Defense (DOD) / SSC contract entitled "High Barrier Non Foil Packaging Structures for Extended Shelf Life." Pliant is exploring a five to seven layer film structure produced via blown film coextrusion, which could potentially produce a single web capable of meeting the barrier and abuse requirements of MRE packaging components.[9]

Chaotic Advection/Smart Blending

Polymer blends are comprised of two or more immiscible polymers, whereby the proportion of each polymer, as well as the resulting blend morphology defines the properties of the resulting blend. Similarly, in composite materials it is the arrangement of the solid additives that define the properties. Conventional polymer blends and composites are not optimized in regards to structure, properties, and composition, due to blending processes based solely on mixing, such as batch mixers and twin screw extruders. Smart Blending, on the other hand, has the ability to control in situ structure development in polymer blends and composites, resulting in programmable morphology development.[10] A SmartBlender is a continuous blending device that has the ability to create polymer blends with novel properties by folding the two melts together, rather than distributing one throughout the other. This equipment was developed by the Department of Mechanical Engineering at Clemson University. The SmartBlender uses a principle of fluid dynamics known as chaotic advection to fold a masterbatch or other components into a matrix polymer. Folding materials together forms a variety of controlled and repeatable polymer morphologies, including: multilayer, single phase continuity (e.g. selective permeability), dual phase continuity (interpenetrating blends), platelet and ribbon, fibrous, droplet, and percolating.[10,11] Figure 6 shows selected morphologies produced via smart blending: (a) percolating morphology, (b) platelet morphology, (c) droplet morphology, (d) highly multi-layered morphology.[10]

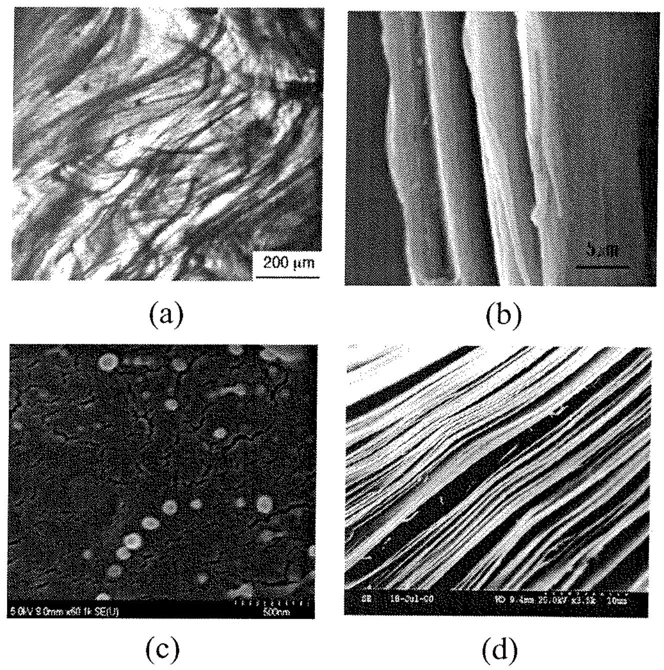

Figure 6. Select Morphologies Produced from Smart Blending[10]

Recent studies by Clemson University have focused on the relation of oxygen permeability to various morphologies produced with Smart Blending technology. Extruded films, consisting of EVOH, LDPE, and maleic anhydride modified polyethylene (MA-PE), were studied to determine which morphology produced the best barrier to oxygen. A clear association between structure and permeability was apparent, with optimal barrier properties seen in a novel single phase continuous and mechanically interlocking morphology. Barrier properties were similar to those obtained with a conventional co-extruded film, and were reduced by a factor of five in comparison to films composed of only LDPE. Interestingly, films produced via chaotic mixing had maximum barrier improvement in structures without MA-PE.[12] Elimination of MA-PE is equivalent to removing the tie layer in a conventional multilayer film, which could potentially allow for down gauging of the film structure, without a loss in barrier properties. However, further research would be required to determine how this affects mechanical properties. Appleton, in collaboration with Clemson University, will explore chaotic advection as a means to produce non-foil based substrates with high barrier and improved mechanical properties under a pending DOD / SSC contract entitled "Improved Barrier Properties of Polymer Substrates for Extended Shelf Life for Food Packaging".

Future Directions

The majority of these technologies are in the research and development stages and show promise in the area of high barrier non-foil packaging for military rations. In the field of nanocomposites, improvements in barrier and mechanical properties have been seen in LDPE and EVOH with the addition of MLS. These systems are in the process of being scaled up to determine if pilot size runs will offer the same property improvements as laboratory scale. To further advance this technology EVOH nanocomposites are being incorporated as the barrier layer of multilayer films, in an attempt to develop a film structure that meets the specifications for MRE packaging. EVOH's sensitivity to moisture is a crucial hurdle that must be overcome in this development. Future work on multilayered structures incorporating retortable grades of EVOH and polypropylene (PP) is also planned. Prototype Meal Bags incorporating a LDPE nanocomposite have been fabricated using films manufactured on pilot scale equipment. The films used in these bags are approximately 50-75% thinner, and are currently undergoing insect testing to determine if thinner nanocomposite films can prevent insect penetration and infestation. A major challenge in nanocomposite research is fully understanding how morphology affects properties such as barrier.

Commercially available coatings have been shown to meet the oxygen barrier requirements for the MRE. Mechanical testing is required to determine if coatings, such as SiOx, will meet the mechanical requirements of MRE packaging. Stress cracks and delamination issues are common since this type of coating is essentially a thin layer of glass. New advances in processing techniques claim to improve mechanical properties of these coatings.

Encapsulated PVDC is a new technology in the United States, however the novel processing technique shows promise in producing non-foil films that do not encounter property loss in humid environments. A PVDC based structure would be ideal for a retort application, since it would not experience "retort shock". One challenge facing this material is recycling issues, which could pose a problem from the military's waste reduction point of view.

Chaotic advection is a novel mixing technique allowing for programmable morphologies in polymer blends and composites. Studies at Clemson University have found correlations between processing parameters and morphology, as well as between morphology and properties such as permeability. Use of this technique to produce high barrier structures will be underway through a pending DOD / SSC funded project with Appleton and Clemson University.

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