Activities Report. Research and Development Associates 42(1): 76-79 (1990)

HIGH BARRIER POLYMERIC MATERIALS FOR INCREASED SHELF LIFE

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The Subsistence Protection Branch and, more specifically, the Experimental Packaging Section, at Natick has been focusing on new barrier plastics for use in a broad range of military applications. Ongoing efforts in three critical areas are utilizing increased shelf-life polymeric packaging materials: The Thermostabilized Meal Tray (TMT), Polymeric Tray Pack, and Flexible Lightweight Polymeric Material. Results of these efforts may have the potential for widespread applicability for the commercial sector as well. My hope is that today's thoughts will lead to even more cooperative efforts in areas of high-barrier packaging interests.

The Thermostabilized Meal Tray (TMT) is a shelf stable, fully prepared meal that was developed to improve foodservice at remote sites where it is difficult to prepare or deliver hot meals. Potential users of the TMT include Air Force Missile Support Crews, security forces, Army Combat Vehicle Crews and designated units of the Infantry Division. The TMT, at present, consists of individual meal components in retortable polymeric trays that nest inside a compartmented tray, covered by a friction fitting lid. The meals may be heated in microwave, immersed in hot water or heated in a vehicle fabric ration heater. The meal containers are constructed of a multilayer coextrusion of high barrier polymeric materials. The outer layers are composed of polypropylene and the middle layer provides barrier properties. The barrier material used is either ethylene vinyl alcohol copolymer (EVOH) or polyvinylidene chloride copolymer (PVDC), since these offer the lowest oxygen permeabilities of the extended shelf life materials available. The containers are sealed with a three-ply laminate material consisting of a polyolefin film, aluminum foil, and polyester.

As an extension of the TMT effort, and in pursuit of the ultimate goal of the project, Natick is working in conjucntion with Rutgers University to develop a compartmented polymeric tray which would allow the simultaneous thermoprocessing of different food components. To accomplish this, they are looking at tray materials with various heat transfer properties or a method to retard heat transfer selectively.

The primary high-barrier resins being used are polyvinylidene chloride copolymer (PVDC) and ethylene vinyl alcohol copolymer (EVOH). EVOH accounts for 70 to 75% of the barrier resins used in retortable containers. It has the best oxygen barrier when dry, but is inherently moisture sensitive. Permeability has been reported to increase by a factor of one hundred when packages containing an EVOH barrier layer are subjected to retorting. It eventually will regain its barrier properties subsequent to retorting, but the product is not fully protected during the interim. This problem is compounded when the outside of the package also contains a good moisture barrier. The EVOH will not be able to shed the trapped moisture. One solution calls for the incorporation of drying agents in the structure of the container to limit the moisture absorption of the EVOH layer. Another possible solution, as patented by one converter, is the replacement of the outer polypropylene layer with polycarbonate. Polycarbonate has high impact resistance, high heat tolerance, and affords a lower moisture barrier than polypropylene, thus allowing the moisture in the EVOH layer an easier and faster exit pathway.

PVDC denotes a copolymer of vinyl chloride and vinylidene chloride. Pure PVDC homopolymer yields a stiff film which is unsuitable for packaging use. When combined with vinyl chloride, a soft, tough, and relatively impermeable structure results. PVDC is a good oxygen barrier that is unaffected by moisture. However, due to its thermal instability, it is difficult to remelt scrap coextruded sheet containing PVDC barrier for recycling purposes.

Apart from the TMT program is a separate effort to develop a polymeric tray pack. The tray must be sufficiently rigid to support the product load and must be lightweight, economical, easily producible, and microwaveable. A two-phase contract was awarded to Springborn Labs to determine feasibility in phase 1 and in phase 2 to produce 1000 polymeric tray packs that are half steam table size, retortable, and able to withstand rough handling requirements. Three different designs were evaluated in phase 1. A ribbed bottom tray was selected because of its superior post retort rigidity. The tray material is 60 mils thick and is composed of filled polypropylene outer layers, EVOH middle barrier layer and desiccated tie layers in between. The lidstock is made of proprietary material which uses PVDC as a barrier. The tray pack has a 100 ounce capacity and an 18 month shelf life.

In support of the TMT and Polymeric Tray Pack programs, the military criteria for retortable plastic packaging includes the following:

Processing	Containers and lids must withstand retorting without delamination or excessive distortion.
Durability	Materials must withstand military rough handling requirements. Although easy-open, peelable lids would be preferred, these do not withstand internal pressure tests.
Barrier (Shelf life)	Military shelf life requirements are a minimum of three years at 70°F. We are not aware of any commercially available polymeric containers that meet this requirement.
Method of Heating	Presently, the TMT and Polymeric Tray Pack are not capable of being heated in a conventional oven. Dual ovenable trays, such as CPET, do not meet our shelf life requirement.

In addition to the TMT and Polymeric Tray Pack, there is an ever present need for a high-barrier, nonfoil, flexible polymeric material that will provide extended shelf life. The material must be retortable and have low oxygen and water vapor permeability.

Transmission rates required are:

O_2	0.05-0.10 cc/mil/100 in^2/24 hr/ATM
H_2O	0.025-0.05 g/mil/100 in^2/24 hr @100°F, 90% RH

It must also be impermeable to grease and oils. Additional secondary characteristics such as biodegradability and use of the material as a fuel are also desirable. Dow Chemical was recently awarded a 6 month contract to develop a nonfoil packaging material to meet our requirements. They are investigating a multilayer coextruded film that combines polypropylene and PVDC (Saran[R]) in a unique way. The film will provide a superior oxygen and water vapor barrier without the need for a secondary moisture barrier layer to protect it during retorting. Film samples produced to date have typically been 5 to 8 mils in thickness and have exhibited excellent physical properties, including tensile strength, elongation, Spencer impact strength and Elmendorf Tear strength. Oxygen transmission rates of less than 0.07 cc/mil/100 sq in/24 hrs after retort are typical. Retort testing of the film at temperatues of up to 275°F for 1 hour has resulted in no delamination of the film structure. Initial Dow testing has also shown the film to pass the requirements of FDA regulations. Evaluations are underway at Natick to fabricate the film into pouches, then fill with food and retort under standard conditions. Another converter has supplied us with proprietary film that is a barrier coated polyester that may be used for retort pouches or lidstock for polymeric trays or TMTs. This film is currently being evaluated.

The ideal nonfoil barrier resin used in films such as this should be readily recycleable without the need for special equipment, retain its performance properties under conditions of high heat and moisture, and can be coextruded with volume thermoplastics or engineering polymers. Although this resin does not yet exist, research of high-barrier polymeric materials has been expanding rapidly and will continue to grow through the 90's.

We know that foil provides the barrier properties for the flexible pouch and offers many advantages. It provides the best overall barrier properties. It is relatively easy to convert and is available in a variety of thicknesses to meet specific packaging requirements. It does, however, have several disadvantages. It has pinholes which can be enlarged during converting and packaging. It is suspect to stress and flex cracks during handling. These pinholes and flex cracks affect barrier properties of the foil. Foil requires more heat to be driven through the package to affect a heat seal and also requires a heat seal layer and a protective layer. These drawbacks have lead to the development of coextruded polymeric containers using high-barrier resins.

What does the future have in store for us? Perhaps a more significant obstacle in the use of high-barrier polymers is its limitations with regard to shelf life. Currently, high-barrier resins do not provide sufficient barrier for the military's requirement of 3 years at 70°F. Increased protection, either by the development of superior barrier resins, or alternative combination of existing materials to form new structures will be needed to fulfill these requirements.

It has been predicted that within the next few years there may be a totally new spectrum of barrier materials based on polymers that are not now being considered for use in shelf stable packaging. Liquid crystal polymers (LCPs), acrylics, copolyesters and fluorocarbons are some of the resins being reformulated to qualify as superbarrier materials of the future. Each has an inherent and individually desirable characteristic--like high heat resistance or less permeable molecular structure--that is being fine-tuned in order to yield better performance and economics for barrier packaging applications. These new developments dramatically increase options when selecting high-barrier resins. Currently, choices are made between the recyclability of EVOH or the moisture resistance of PVDC.

General Electric is developing methods to enhance barrier properties of medium-performance amorphous nylon materials for use in high temperature engineering coextrusions. Similarly, Allied-Signal is developing ways in which to use fluorocarbons as high-temperature, high-barrier coextruded layers. Mitsubishi has also introduced its MXD6 nylon as a barrier resin. This resin is used commercially in Japan for retortable packages. Rohm and Haas is evaluating its experimental resin XHTA for retortable packaging. This structurally stiff barrier resin demonstrates strong adhesion to polycarbonate, nylons and polyesters without the use of tie layer adhesives.

Advances in tie layer development have increased options with respect to the selection of a barrier resin. These adhesives are designed to bond structural resins to barrier resins more securely against the possibility of delamination during retorting. Exxon has developed a new tie layer resin with increased tenacity and peel strength. These characteristics are maintained under the high-temperature, high moisture conditions that are routinely encountered in processing PP/PVDC based containers. Himont and Mitsui Petrochemical are similarly active in developing heat resistant tie layer to bond PP and PVDC with a bond strength equal to the EVOH tie layers.

In closing, the ongoing projects discussed today utilizing high-barrier polymer materials, such projects as the TMT, Polymeric Tray Pack and the "magic" film can only be enhanced by advancement in the state-of-the-art. It is my hope that the commercial sector will continue to come forward as it has in the past to work cooperatively with the scientist and engineers at Natick and that the end-product of this dialogue and effort will be high-barrier polymeric materials that will protect the food of the student sitting in the warmth of the cafeteria as well as the food of the soldier huddled on the battlefield.