SURVEY OF METHODS FOR ACHIEVING LOW GASOLINE FUEL-PERMEATION

IN ROTATIONALLY-MOLDED ARTICLES

A Paper
Submitted to the Graduate Faculty
of the
North Dakota State University
of Agriculture and Applied Science

By

Brent Alan Nerenz

In Partial Fulfillment of the Requirements
for the Degree of
MASTER OF SCIENCE

Major Department:
Mechanical Engineering

October 2018

Fargo, North Dakota

North Dakota State University
Graduate School

Title

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MASTER OF SCIENCE

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ABSTRACT

The establishment of governmental regulations on the evaporative emission performance of fuel system components has caused molders and their material suppliers to develop innovative materials and processes by which to meet such requirements. Rotational molding is a common processing choice for fuel containers given its ability to produce complex, hollow geometries with consistent wall thickness. A number of strategies have been devised for meeting fuel permeation requirements in rotationally molded containers, each demonstrating significant benefits and detriments to the processor. Single, homogeneous materials have difficulty in simultaneously providing adequate fuel permeation, durability, and affordability. The ability of rotational molding to create containers having a plied, multi-polymer architecture allows molders to create articles which exhibit exceptional performance in each aspect. Multi-layer processing creates unique challenges for the rotational molder; however, different technologies have been demonstrated which enable multi-layer articles to be produced from a single material introduction, thereby maximizing processing efficiency.

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CHAPTER 1. ROTATIONAL MOLDING OF FUEL CONTAINERS

A fuel tank constructed from a polymer source offers a number of advantages when compared with traditional metallic designs. Weight, durability, and corrosion-resistance are all superior in polymer tanks, and the formability of plastic allows the designer to create complex tank geometries with relative ease[1]. For these reasons, polymeric fuel tanks have become the preferred choice for fuel containment in vehicle and equipment platforms.

Rotational molding has been demonstrated as a primary processing method by which polymeric fuel tanks can be made for the lawn and garden, heavy equipment, marine, and off-road recreational vehicle markets. In comparison to blow molding, rotational molding can be used to create relatively more complex geometries having uniform wall thickness and minimal residual stress. However, the cycle time required to form a single part in rotational molding is an order of magnitude greater than that of blow molding. This low throughput prevents rotational molding from being considered for goods requiring high-volume production, namely the polymeric fuel tanks currently utilized by the automotive industry[2].

Commercial fuel tanks have two primary requirements in that they must withstand applied stresses and impact loads without exhibiting catastrophic failure, and that their construction must be able to withstand the chemical attack and ingress of the fuels they contain. Fuel tanks are typically exposed to low values of static stress through mounting and confinement, and experience low levels of both positive and vacuum pressures during service. However, fuel tanks are also used in applications in which they are mounted on the exterior of a unit or are tightly constrained within a chassis and experience vehicle impact and vibration. It is therefore expected that fuel tanks exhibit sufficient ductility and impact strength, as the fracture of a fuel-containing vessel poses a significant safety risk. The chemical stability of a fuel tank and its ability to resist fuel ingress and property degradation is an equally important consideration. Fuel tanks should be constructed from materials that do not exhibit

embrittlement from exposure to hydrocarbons or alcohols, as well as those which possess sufficient barrier properties to gasoline and diesel formulations.

Regulatory Requirements for Evaporative Fuel Emissions of Fuel Containers

The permeation of gasoline through the structure of a polymeric fuel tank requires important scrutiny, as emitted vapors pose both environmental risk and safety risks to the end user. Regulatory oversight has been established at the federal and state government levels which qualify material systems and components with regard to their permeability performance. Requirements for evaporative emissions vary based on the platform in which the tank will be used, and some are further differentiated based on the displacement or maximum power of the paired engine. These factors dictate whether or not evaporative emissions are specified as permeation rates seen at the tank-level, or diurnal rates seen at the fuel system-level. Permeation rates correspond to the amount of fuel lost through the structure of the tank itself, and are typically expressed with units of 'mass per unit of internal surface area per day'. Diurnal emission rates correspond to the fuel loss that is seen through tank permeation as well as in vapor loss due to temperature fluctuations experienced in every-day use, and are expressed with units of 'mass per volume of container capacity per day'. Diurnal testing is conducted in the presence of any device which transports or captures fuel vapor, such as venting mechanisms, vent lines, and carbon cannisters, whereas permeation testing is conducted on individual fuel component such as tanks, fuel lines, and fill caps. The choice of tank material is primarily responsible for determining a fuel permeation rate, whereas it is only a contributing factor to the overall diurnal emission rate of a fuel system.

The Environmental Protection Agency (EPA) requirements for fuel tank evaporative emission performance is contained within the Code of Federal Regulations (CFR) under Title 40: *Protection of the Environment*. Chapter I, Subchapter C, Part 86: *Control of Emissions from New and In-Use Highway Vehicles and Engines,* contains evaporative emission requirements for on-road automotive applications; however, these requirements will not be

examined as they do not pertain to fuel tanks typically created using a rotational molding process. Subchapter U, Part 1060: *Control of Evaporative Emissions from New and In-use Nonroad and Stationary Equipment* provide requirements for polymer tanks more commonly produced through rotational molding.

Section 1060.103 summarizes and unifies permeation emission requirements for marine, recreational vehicle, and 'small' spark-ignition (SI) fuel tanks. An evaporative limit of 1.5g/m²/day is required when permeation testing under the conditions of Section 1060.520. A limit of 2.5g/m²/day has also been established when the permeation test is carried out at elevated temperature (40°C) in order to better represent in-use conditions. The distinction between a 'small' and 'large' SI fuel tank is made by considering the engine to which it is paired. 'Small' SI fuel tanks are used to supply engines exhibiting maximum power of 19kW (approximately 25.5hp) or less, whereas 'large' SI fuel tanks supply those exceeding 19kW. Marine and 'large' SI fuel tanks are also subject to diurnal emissions requirements. Marine fuel tanks may not exceed 0.053g/L/day losses when tested under 1060.525, whereas 'large' SI fuel tanks must not exceed 0.106g/L/day when tested under 1048.501. EPA evaporative emission requirements which pertain to fuel tanks typically manufactured using the rotational molding process are summarized in Table 1[3-4]:

Table 1.   EPA Evaporative Emission Requirements for Rotationally-Molded Fuel Tanks

Vehicle Platform	Permeation Rate g/m²/day	Permeation Method	Diurnal Rate g/L/day	Diurnal Method
Recreational	1.5	CFR 1060.520[a]	-	-
'Small' SI	1.5	CFR 1060.520	-	-
'Large' SI	-	-	0.053	CFR 1048.501
Marine	1.5	CFR 1060.520	0.106	CFR 1060.525

[a]   CFR 1051.515 is an accepted alternate test method

The California Air Resources Board (CARB) has also specified the required evaporative performance of fuel tanks sold or operated within the state of California. Unique requirements and test procedures have been established for the categories of recreational vehicles, marine watercraft, and small off-road equipment. Large off-road equipment, however, is specified as being governed under EPA requirements.

Chapter 9, Article 3, of Title 13 of the California Code of Regulations specifies the evaporative emission performance of off-highway recreational vehicles. For 2018 model year and later vehicles, a diurnal emission rate of less than 1 gTOG/day is required when qualified under test protocol TP-933[5]. TOG refers to *Total Organic Gasses* or all emitted carbon-containing gasses with the exception of carbon monoxide and carbon dioxide.

Chapter 15, Article 1, of Title 13 of the California Code of Regulations specifies the evaporative emission performance of off-road vehicles having engines under 19kW maximum horsepower. The emission requirements are further classified based upon the engine displacement D to which the fuel tank is paired. For engines having maximum displacement of less than 80 cubic centimeters (cc), only a maximum permeation rate is specified. This value is 1.5 g/m²/day when tested under TP-901. For engines exceeding 80cc displacement, a maximum permeation rate of 1.5 g/m²/day is specified; diurnal rates are determined from considering both the displacement class of the engine as well as the nominal capacity of the fuel container when measured in liters, L[6].

Chapter 15, Article 1, of Title 13 of the California Code of Regulations specifies the evaporative emission performance of spark-ignition marine watercraft with gasoline-fueled engines. For paired engines having less than 30kW maximum power P, evaporative emission rates are aligned with EPA requirements and are tested similarly (CFR 1060.520 and 1060.525). For engines exceeding 30kW maximum power, a maximum tank permeation rate of 0.7 g/m²/day has been specified for model year 2018 and beyond. This rate must be measured in accordance with TP-1504. Several options exist for qualifying the maximum allowable diurnal

emission rate, given the overall size of the watercraft as well as the componentry selected for carbon vapor capture. However, the diurnal performance may be qualified under an alternative process, irrespective of size and componentry if tested under TP-1501[7]. CARB evaporative emission requirements which pertain to fuel tanks typically manufactured using the rotational molding process are summarized in Table 2:

Table 2.   CARB Evaporative Emission Requirements for Rotationally-Molded Fuel Tanks[5-7]

Vehicle Platform	Permeation Rate g/m²/day	Permeation Method	Diurnal Rate g/day	Diurnal Method
Recreational	-	-	1.0	TP-933
Small Off-Road $D<$80cc	1.5	TP-901	-	-
Small Off-Road 80$< D <$225cc	1.5	TP-901	0.95 + 0.056L	TP-902
Small Off-Road $D>$225cc	1.5	TP-901	1.20 + 0.056L	TP-902
Marine $P>$ 30kW	0.7	TP-1504	0.97 + 0.048L	TP-1501

Evaluation of Fuel Tank Emission Performance

Evaporative emission performance must be demonstrated under the test protocols established by EPA and CARB requirements. Fuel permeation testing will be described in-detail, whereas diurnal testing will be examined only in the context of fuel tank performance.

Applicable fuel permeation test protocols (CFR 1060.520, TP-901, and TP-1504) each contain three basic elements: a series of durability tests, a preconditioning fuel soak, and a test evaluation. Durability tests are designed to simulate in-service conditions and ensure that any barrier technology utilized in the tank design will not degrade, erode, or lose permeability performance during its service life. Cyclic pressurization and slosh testing are used to create wall stresses and are used to assess the mechanical durability of the material system under fatigue loadings. Exposure to ultraviolet radiation (UV) is also required in order to assess the

weatherability of the material system. Table 3 summarizes the test conditions required for each fuel permeation test protocol.

Table 3.   Durability Test Conditions for Fuel Permeation Testing[3,8-9]

Test Protocol	Cyclic Pressurization	Fuel Slosh	UV Exposure
EPA CFR 1060.520	-3.4/+13.8 kPa at 60Hz 10,000 Cycles	Test Fuel at 40-50% of Capacity -15° to +15° at 0.25Hz 1,000,000 Cycles	≥24 W/m² for 450hr
CARB TP-901	-3.4/+13.8 kPa at 60Hz 10,000 Cycles 49±3°C Environment	Test Fuel at 50% of Capacity -15° to +15° at 0.25Hz 1,000,000 Cycles	≥24 W/m² for 450hr
CARB TP-1504	-3.4/+13.8 kPa at 60Hz 10,000 Cycles	Test Fuel at 40-50% of Capacity -15° to +15° at 0.25Hz 1,000,000 Cycles	≥24 W/m² for 450hr

The preconditioning fuel soak is used to ensure that the fuel container becomes fully saturated prior to the recording of test data. The EPA has specified the use of E10 gasoline as the test fuel, as described under 1065.710[10]. This fuel has a nominal ethanol content of 9.6-10.0% by volume and an octane rating of 87-88. CE10 may also be used as an alternate test fuel; its volume composition is a hydrocarbon mixture of 45% isooctane, 45% toluene as-referenced as *Fuel C* in ASTM D471[11], which is then blended with 10% ethanol. TP-901 specifies the use of either E10 test fuel or LEV III Certification Gasoline, a blend containing 9.8-10.2% ethanol by volume with composition as-specified in Title 13 of the California Code of Regulations[12]. TP-1504 specifies the use of CE10 or E10 CERT fuel which has equivalent composition as the LEV III Certification Gasoline.

Under the conditions of CFR 1060.520, the preconditioning fuel soak is performed by filling the test tank to nominal capacity, sealing it, and allowing it to soak at 28±5°C for 20 weeks. An elevated temperature condition of 43±5°C may also be used in order to shorten the soak time to no less than 10 weeks. TP-901 requires the fuel soak to occur in an ambient

environment of no less than 38°C for a minimum of 140 days and TP-1504 follows the requirements of CFR 1060.520.

The test evaluation for CFR 1060.520 is performed by determining the mass loss of a sealed, fuel-containing tank over a 10-day period. Following the preconditioning soak, the tank is emptied, refilled to nominal capacity with test fuel, and sealed after it reaches an equilibrium temperature of 28±2°C. A second, reference tank with equivalent geometry and no prior exposure to the test fuel is then filled with an inert material until its mass is approximately equal to that of the test tank. The initial difference in mass between the test and reference tanks is determined before placing the test tank in a 28±2°C environment for the duration of the test. The test tank is then removed once daily for weighing with the reference tank being used to tare the balance. After 10 days of measurement, the cumulative weight loss is calculated for each day and normalized by the internal surface area of the tank. A linear regression of cumulative weight loss versus test day provides the permeation rate and the test is considered valid if a coefficient of determination exceeding 0.95 is observed[3].

TP-901 specifies that the test protocol and mass loss determination must be carried out on five equivalent test tanks. It proceeds in near-equivalent manner to CFR 1060.520, although a 40±2°C environment is used throughout. The daily permeation rate is calculated and reported for each tank along with its corresponding mean rate and 95% confidence interval upper limit. The final permeation rate is also determined by dividing the total cumulative mass loss by the total number of test days[8]. TP-901 also provides the option of determining the permeation rate through the use of a flame ionization detector (FID). This test is carried out at 40±2°C in a sealed enclosure and is performed over 24 hours. Calculation of the permeation rate follows Section 4 of TP-902. TP-1504 follows CRF 1060.520, requires a single tank to be investigated, and does not allow for an FID determination.

Diurnal emission test protocols require that a fuel system be exposed to temperature fluctuations which typify in-service use. Fuel vapors which permeate the fuel tank, lines, and

vapor containment system are collected and analyzed to determine the overall diurnal emission rate. This testing is known as a Sealed Housing Evaporative Determination (SHED) and involves placing the fuel system in a sealed environment and monitoring the concentration of emitted hydrocarbon vapors through the use of FID or gas-phase chromatography.

CFR 1060.525 specifies the test procedure for the diurnal testing of marine fuel tanks under EPA requirements. It requires that a fuel system be exposed to three, 24hr temperature cycles over which emissions rates are determined. Ambient or fuel temperatures are specified for each hour throughout the 24hr period and are determined based on the intended use of the fuel system. For example, installed marine fuel tanks must have their fuel temperature cycled between 25.6°C and 32.2°C. The fuel tank is filled to 40% nominal capacity with E10 fuel and the system is stabilized by subjecting it to an initial temperature cycle. The test begins after completion of the stabilization cycle, and emissions are sampled for each subsequent 24hr. period. The highest observed 24hr emission rate is chosen as the reported test result. If the permeation rate of the fuel tank is known and the test tank used for diurnal testing was preconditioned under 1060.520, then the emissions contributed from tank permeation may be subtracted from the reported diurnal emission rate[3]. CFR 1048.501, which specifies diurnal emission testing for large, spark-ignition fuel system, follows the structure of CFR 1060.525; however, it requires that tanks be durability-tested and preconditioned under the requirements of CFR 1060.520 and does not allow for permeation rates to be subtracted from the overall diurnal emission rate[4].

TP-902 specifies the test procedure for diurnal emission testing of small off-road fuel systems under CARB requirements. It differs primarily from EPA testing procedures in that it requires that the fuel system be connected to its corresponding engine and that the engine be operated prior to enclosing the fuel system in the SHED environment. The test begins by subjecting the test tank to the pressure cycle and fuel slosh durability tests specified in TP-901; UV testing is only required if the system is to be exposed in the overall design of the vehicle. The

tank is then mated to the engine and filled to nominal capacity with LEV III or E10 test fuel. A preconditioning fuel soak is performed by running the engine at maximum governed speed for five minutes and refilling the tank thereafter. The fuel system is then soaked at 30±10°C for no less than 140 days. After the preconditioning period, the tank is drained and refilled to 50% capacity before operating the engine at maximum speed for fifteen minutes. The fuel system is then placed within the SHED enclosure and experiences an additional one hour of *hot soak*, at 35°C. Vapor emissions are collected during this time period and are reported as the hot soak emission rate. The enclosure is then gas purged and cooled to 18.3°C before the 24hr diurnal test is started. The 24hr diurnal test is conducted by applying the time-dependent temperature profile (18.3-40.6-18.3°C) throughout the enclosure and measuring the amount of emitted hydrocarbon and ethanol vapors[13].

TP-933 is used to determine diurnal emission rates of recreational vehicles such as all-terrain vehicles and off-road motorcycles. It differs primarily from TP-902 in that it allows for diurnal emission to be collected over three 24hr periods by fluctuating the ambient temperature between 22 and 36°C, or during a single 24hr period by maintaining a constant temperature of 30±2°C. For a steady state temperature test to be valid the vapor containment device (i.e. carbon cannister) must be have demonstrated performance of less than 0.5% emission bleed and the venting system must have no less than a 13.8kPa relief pressure[14]. TP-1501 specifies the test conditions for determining diurnal emission rates in spark-ignition marine engines. It differs primarily from TP-902 in that the hot soak is performed at 41°C. Durability testing is also required under this protocol; however, the requirements are non-specific and must be proposed by the manufacturer. Proposals are written by the applicant and consider test conditions which are representative of in-service use; approval for testing is granted by CARB[15].

Evaluation of Fuel Tank Durability

The material system chosen for a fuel tank's construction should exhibit sufficient strength, ductility, impact resistance, and flame retardancy in order to withstand pressure, vibration, wear, impacts, and exposed flames. The rotational molder is challenged by the lack of established test standards for material performance of molded articles and relies primarily on the *Association of Rotational Molders'* Low-Temperature Impact Test to evaluate materials and perform quality control on processing. The designer must consider both the material system as well as the fuel tank geometry in creating an adequate design, and must demonstrate conformance to any applicable regulatory requirements on fuel tank durability.

The Low-Temperature Impact Test Method[16] utilizes falling dart impact to characterize the performance of molded articles. Reported outcomes of the test include the average Mean Failure Energy exhibited by the material as well as the failure type(s) found to occur. Ductile failure is reported when the dart punctures through the test coupon, leaving the coupon intact, whereas brittle failure is described by fragmentation of the coupon into two or more separate pieces.

The test is carried out by performing successive drops of a tup of known weight w (4.5, 6.8, 9.0, or 13.6kg) from known heights onto 127mm square specimens cut from molded articles and exhibiting thickness between 3.2 and 6.4mm. Specimens are unconstrained from lateral movement and are supported only in the direction of impact by a flat support having a 89mm diameter open center. Specimens are cut from molded articles and oriented so that the outer surface (i.e. that which contacted the mold wall) is facing upward. If testing is carried out at reduced temperature the specimens should experience a minimum two-hour soak at temperature if placed loosely with full surface circulation. A full 24hr soak at temperature is required if the specimens are stacked together.

An initial drop height is determined by the operator and the initial trial is performed. Depending on the result of the current test, the next immediate test height is determined by

increasing the height one increment Δh in the event of a non-failure, or reducing by one increment in the event of a failure. The test proceeds in this manner until the test set is exhausted; a total sample set of 20 plaques is recommended by the standard to ensure a valid test is performed. After completion of the test, the total number of non-failures is counted, as well as the total number of failures. Whichever is found to occur less frequently is known as the test event, and the total number of these incidences is designated as N. The lowest height at which the event first occurred is designated as h_o.

The mean failure energy $\bar{E}$ is determined by applying Eq.1, where the mean failure height $\bar{h}$ is determined through application of Eq.2. The parameter A is defined by Eq.3, where i is the counting index used to describe the incremental height levels (with h_0 corresponding to $i=0$) and n_i is taken as the total number of events found to occur at the corresponding height level. The determination of addition or subtraction of the constant term is made by considering the failure event, with failures resulting in subtraction and non-failures in addition. An example test record with sample calculations is included as Appendix A1.

$$\bar{E} = \bar{h}w \qquad\qquad\qquad (Eq.1)$$

$$\bar{h} = h_0 + [\Delta h \left(\frac{A}{N} \pm 0.5\right)] \qquad\qquad (Eq.2)$$

$$A = \sum_{i=0}^{k} i n_i \qquad\qquad\qquad (Eq.3)$$

The results obtained under dart impact are influenced by the processing conditions by which the article was created. Articles which are under-processed will contain voids throughout the material cross-section, as the critical temperature required to dissolve much of the entrapped gasses was not met. These voids act as stress concentrators and promote crack propagation under impact. Alternatively, articles over-processed will experience significant levels of oxidation on the inner material layer. The inner layer develops once all powders have sintered and is exposed to the bulk air contained by the mold. The inner layer experiences rapid tensile and shear loadings under impact, and requires material ductility to prevent crack

initiation and arrest crack propagation. Therefore, material characterization using the dart impact method must also demonstrate that a processing relationship exists and that optimal conditions have been determined.

A number of safety standards exist for demonstrating acceptable durability of molded fuel tanks. Voluntary safety standards are drafted through the work of standard organizations and trade groups and establish baseline durability requirements. Examples of standards which pertain to rotationally-molded fuel tanks include: ANSI/OPEI B71.10-2013 (Off-Road Outdoor Power Equipment) ANSI/SVIA 1-2017 (Four Wheel All-Terrain Vehicles), and ANSI/ROHVA 1-2010 (Recreational Off-Highway Vehicles). For marine fuel tanks, safety requirements are compulsory and are found in CFR Title 33: *Navigation and Navigable Waters*. Chapter I, Subchapter S, Part 183: *Boats and Associated Equipment*.

CFR 183.510 summarizes the durability requirements for marine fuel tanks and specifies the required qualification tests given the volume of the tank. For each tank geometry a design pressure is specified by the manufacturer, which represents the maximum pressure the tank can withstand without experience fuel leakage. A static pressure test in which no air leaks are observed at the design pressure is required for all tank geometries. Additionally, all tank geometries are required to demonstrate non-leak integrity after being subjected to the fire test described by 183.590. In this test a tank is secured in a fire chamber and is subjected to a 2.5min burn. A pan containing heptane is placed 8-10in below the tank and ignited; the tank must experience a temperature of 648°C within one inch of its surface for the test to be valid. Tanks having capacity under 25gal must demonstrate non-leak integrity after being subjected to a shock test as described in 183.584. Depending upon the placement of the tank within the watercraft, the tank is either subjected to 1000 cycles of 15 or 25g vertical acceleration, applied at 80Hz or less. The tank first undergoes a fuel soak at 50% for 30 days at 21°C before draining the fuel and filling the tank to nominal capacity with water for the purpose of testing. Fuel tanks exceeding 94L capacity must demonstrate non-leak integrity after being subjected to a pressure-

impulse test as specified in 183.586. The tank undergoes preconditioning equivalent to that described in 183.584 and is filled to capacity with water prior to the test. 25,000 pressure impulses of 0 to +20.7kPa to 0 are applied to the tank at a rate of no greater than 0.25Hz through the means of an air source entering the top of the tank. Tanks exceeding 200gal of capacity must also undergo a fuel slosh test and demonstrate non-leak integrity thereafter. This test is performed after the shock and pressure-impulse tests and involves rocking the tank between -15°and +15°C for 500,000 cycles at a rate of 0.25 to 0.33Hz[17].

Summary of Fuel Tank Requirements

Rotational molders must be capable of providing fuel tank constructions which meet governmental regulations for evaporative emission performance, as specified by the United States Environmental Protection Agency and the California Air Resources Board. Required performance levels are based on the vehicle platform in which the tank will be used and may also be further scrutinized based on the engine displacement of the vehicle. The requirements are either specified as a maximum permeation rate or as a maximum diurnal emissions rate in which the larger fuel system is examined.

A durable material solution is also required to realize adequation permeation performance and gain widespread commercial appeal. Permeation testing protocols incorporate a series of durability tests in which cyclic pressurization, fuel slosh, and UV exposure are used to assess the integrity of the system. Rotational molders use the *ARM Low-Temperature Impact Method* to evaluate material performance and refine processing conditions. Customer durability requirements are inherently variable and may reference performance under the ARM method, conformance to a voluntary safety standard, or a unique internal standard. Durability requirements for marine-based fuel tanks are required by federal statute and include both mechanical integrity and flammability assessments.

It is the goal of the rotational molder to develop a material solution which is capable of meeting all permeation and durability requirements while maintaining high profitability and

commercial appeal. Single-layer strategies are first examined, as they represent solutions which minimize processing complexity and are likely to have the greatest throughput and lowest scrap rate. Multi-layer strategies are discussed next, as they provide a means by which to combine the high-performance aspects of several materials into a single molded article. Two methods for creating multi-layer constructions using a single material introduction are also presented, which represents an optimal scenario in which multi-layer strategies are employed at single-layer efficiencies.

CHAPTER 2. SINGLE-LAYER SYSTEMS AND RELATED METHODS

The single-layer system represents the ideal means by which to achieve low fuel permeation in rotationally-molded articles. Single-layer systems obtain relatively high throughput and are preferred for their ease of processing in comparison to multi-layer architectures. The term single-layer will be used to refer to any singular material system that is introduced during the molding cycle. This includes homogeneous materials with uniform composition, alloyed or reinforced systems which incorporate additional constituents to augment permeation or mechanical performance, as well as post-molding treatments which either transform the material structure or add low-permeation coatings to the molded article.

Fundamental Concepts in Rotational Molding

Figure 1. provides the four primary operations of rotational molding in which material is input into a hollow mold, the mold is heated under rotation, the mold is cooled under rotation, and the molded article is removed. The heating stage involves the tumbling and sintering of plastic particles within the mold which undergoes biaxial rotation to distribute the particles evenly across all mold faces and create a uniformly-thick article. Under rotation the material forms a powder pool which is ideally stagnant and remains at the bottom-most surface of the tool at any time or orientation. As molds are convectively heated the inner mold surface reaches
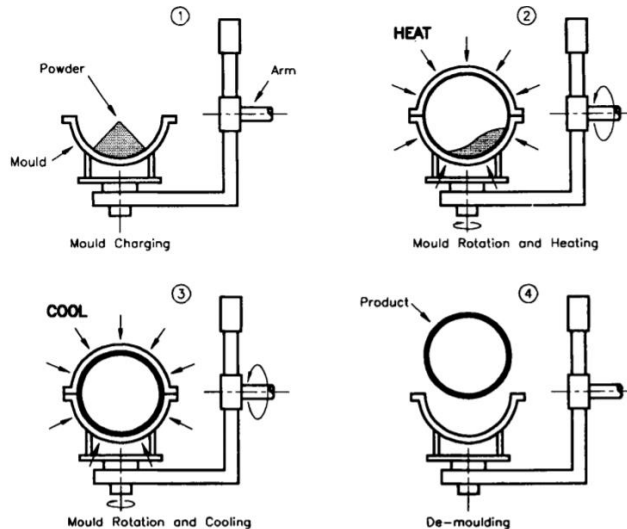
Figure 1. Primary operations in the rotational molding process[18]

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the melt temperature of the polymer causing the particles to adhere and exhibit tack. Successive particles continue to be deposited, gradually building up the material thickness until the bulk powder pool is depleted. The individual particles become a homogeneous structure through melt sintering as additional heat is applied. Particle boundaries are combined and entrapped gasses are dissolved into the melt as the heat flow progresses from the outer to the inner particle layers. As seen in Figure 2, the particles which first adhere to the mold wall undergo sintering and densification while the remaining particles are being deposited. The heating process concludes when all particles have been deposited and the entire thickness is condensed and free of entrapped air voids. This point is determined by monitoring the temperature inside the mold cavity; the *Peak Internal Air Temperature* or PIAT is a parameter used to quantify the cure of the molded part and has been found to correlate well with the impact strength of molded parts. A time-dependent internal temperature trace is seen in Figure 3, with the PIAT represented by the maximum experienced temperature. The temperature trace is also indicative of other key events during the molding cycle: *A* represents the onset of particle deposition whereas *B* represents the full depletion of the powder pool; *D* represents the point at which crystallization has occurred and *E* represents the solidification of the molded article.
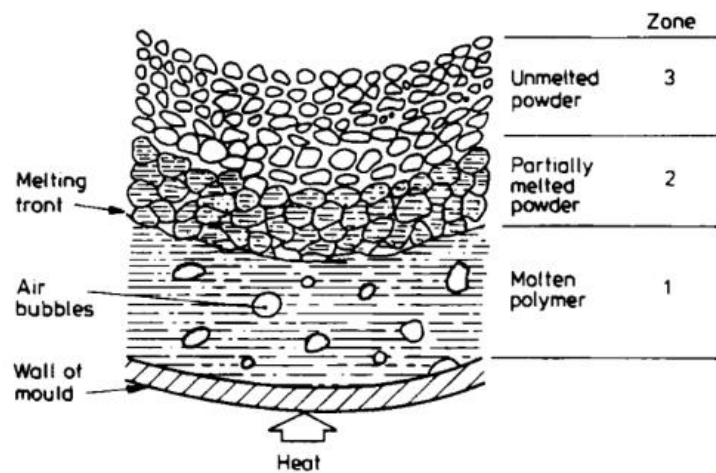
Figure 2.   Progression of particle sintering and densification during molding process[18]
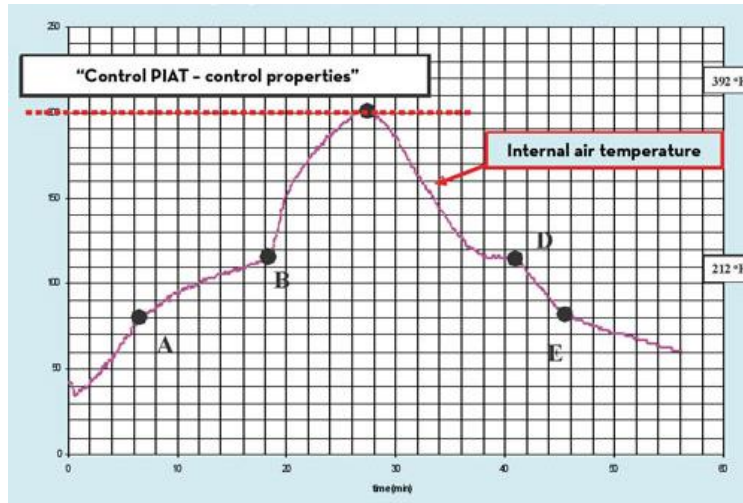
Figure 3. Time-dependent internal air temperature trace for typical molding cycle[19]

The cooling process proceeds similarly in that mold continues to rotate throughout and that convection is the primary means by which heat is transferred. Air or water cooling is possible and can be used at different intervals to control the cooling rate. Polymer crystallization can be controlled in this regard, although aggressive cooling can exacerbate warp in the molded part geometry.

Suitable Materials for Use in Rotational Molding

Rotational molding is able to accommodate a large number of thermoplastic and thermoset resins given its ability to process both dry (granular) and liquid feedstocks. Non-liquid thermoplastic materials are molded in greatest volume and include polyolefins, polyamides, polycarbonates, polyesters, acrylics, styrenics, acetals, fluoropolymers, thermoplastic elastomers, and vinyl chlorides. Liquid material systems such as vinyl-chloride plastisols, polycaprolactams, polyurethanes, epoxies, and silicones have also been demonstrated in rotational molding with commercial success[20].

For a non-liquid material to be rotationally molded with adequate mechanical performance it must be able to be ground into a uniform distribution of fine particles with adequate shape, be able to exhibit sufficiently low zero-shear viscosity, and be able to withstand the heat environment of molding without undergoing severe thermal oxidation. The shape and

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size distribution of ground particles dictates both the dry flow and sintering behaviors of the polymer. Adequate dry flow of the resin is necessary for uniform wall thickness distribution throughout the molded article; resins with a high content of fine particles undergo fluidization and exhibit poor flow characteristics. The size and shape of the ground particles dictates the packing density and thus the void content observed during sintering. Spherical particles or those exhibiting irregularities (i.e. tails) have poor packing density and require longer heat durations for complete void dissolution[20].

The zero-shear viscosity of polymer must be sufficiently low to allow for the dissolution of voids during the sintering process. As sintering progresses and entrapped air coalesces within the melt, the polymer reaches a viscosity at which oxygen and nitrogen become soluble within its structure; this behavior can be described by Henry's Law. The polymer structure begins to accept dissolved gases from the air voids which in turn reduces their size until they are diminished. The dissolution of voids is critical for achieving good mechanical performance[21-23]. Polymers with comparatively higher molecular weights are increasingly more difficult to process in rotational molding, and must be driven to higher temperatures to drive void dissolution while maintaining efficient processing. As higher temperatures are introduced, however, an increase in thermal oxidation is likely. Ultra-high molecular weight polyethylene is an example of a polymer which can only be molded through aggressive heat stabilization due to its high melt viscosity.

Polymers are subjected to aggressive thermal environments during rotational molding and typically spend between 10 and 15 minutes in the molten state. This duration is needed for complete sintering and void dissolution, processes which suffers from the lack of any applied forces during molding. High melt-temperature resins, such as polyamide 6, are successfully molded if formulated with adequate heat stabilization. In contrast, polyamide 6,6 exhibits a melt temperature 30-40°C greater than that of polyamide 6 and is not commonly used for rotational molding. The rotational molder can minimize thermal oxidation by choosing to

introduce an inert gas into the mold, either at the start of the cycle (purging) or at a time during the heating cycle through the use of gas transfer lines incorporated within the primary drive of the molding machine. Inert gas processing, typically performed with nitrogen or carbon dioxide, has been used to mold thermally-sensitive polymers such as cellulosics, acrylics, and styrenics[20]. However, inert gas processing adds cost and complexity to the molding cycle and must be correctly applied and understood to realize its benefits.

One commodity thermoplastic which is difficult to process in rotational molding is Acrylonitrile-Butadiene-Styrene (ABS). The protection of the butadiene phase from thermal oxidation is the primary concern, as it causes embrittlement and poor impact strength in molded articles. Experimental work has found that incorporating plasticizers at significant weight loadings (~15%) is effective at promoting void dissolution at lower temperatures, thereby minimizing thermal degradation. It was also found that by shifting the particle size distribution towards larger particles (i.e. using a lower mesh screen during grinding) that higher impact results could be obtained[24]. It is thought that this creates an overall reduction in particle surface area, in which less of the butadiene phase is exposed to oxidation. ABS can be polymerized using a variety of methods, including emulsion, suspension, and mass polymerization; however, it is estimated that approximately 85% of all ABS produced is done so using an emulsion process[25]. It has been observed that ABS blends created using mass polymerization methods exhibit reduced thermal oxidation[26]. Factors which likely influence this effect include the size and dispersal of the butadiene phase, the amount of grafting on the butadiene chain, as well as the residual amount of contaminant left in the polymer. It is possible that rotationally molded grades of ABS could be commercially developed given the findings mentioned here.

Materials Exhibiting Fuel Permeation Resistance

Vapor transport through a polymer membrane is a process composed of three distinct events: absorption of the gas molecule into the polymer at the interior surface, diffusion of the

gas molecule through the structure, and desorption of the molecule into the atmosphere at the exterior surface. The absorption process is dependent upon surface interactions between the vapor and polymer, and one can examine polarity and functionality of a polymer to help predict whether or not vapor molecules will be drawn into polymer structure. The diffusive component of permeation can be described using a form of Fick's first law of diffusion, represented by Eq. 4, where J is the rate of permeation through a planar membrane of homogeneous composition having thickness t and subject to a pressure differential ($\Delta p \geq 0$), with $\bar{P}$ representing the permeability coefficient of the material/vapor system. The permeability coefficient is found as the product of diffusive D and solubility S coefficients (Eq.5), and the combined examination of Eqs. 4 and 5 presents strategies by which to limit the overall permeation rate[27].

$$J = \bar{P}\frac{\Delta p}{t} \qquad\qquad\qquad\qquad \text{(Eq.4)}$$

$$\bar{P} = D \cdot S \qquad\qquad\qquad\qquad \text{(Eq.5)}$$

There are a number of factors which influence the diffusive and solubility characteristics of fuel vapors moving through the structure of a molded polymer. Polarity and crystallinity are the two primary characteristics of the polymer which affect permeation. The polarity of the vapor molecule as well as the relative size of the vapor in comparison to the interstitial spacing of the polymer represent its primary characteristics. Indirect, or environmental effects such as temperature, humidity, and pressure also dictate permeation performance. For example, an increase of 5°C in ambient temperature has been shown to increase permeation rates 30-50% due to the higher partial pressure of the vapor as well as an increase in its solubility within the polymer[28]. Ambient humidity causes a plasticization effect in hygroscopic materials, which in turn opens the polymer structure and promotes increased permeation.

Polymer crystallinity affects gas permeability in that crystalline domains are tightly packed and discourage the diffusion of vapor molecules through the structure. Amorphous domains facilitate travel of vapor molecules and it has been shown that the solubility of the vapor within the polymer is proportional to the volume fraction of amorphous polymer[29].

Crosslinking also works to fix the polymer structure and discourage permeation, with a higher degree of crosslinking resulting in lower permeation rates.

Much like gasoline itself, emitted vapors are comprised of a blend of several constituent materials. An analysis of headspace gas, that which resides over the bulk fuel in an enclosed fuel tank, revealed the approximate vapor composition for E10 fuel as shown in Table 4[30]. This analysis was conducted through the use of FID and gas-phase chromatography and provides the relative concentration of each constituent based on a parts-per-billion measure of all carbon-containing species. As gasoline vapors are largely comprised of non-polar, hydrocarbon vapors, popular choices for barrier materials include polar, crystalline polymers such as polyamide and ethylene vinyl-alcohol (EVOH).

Table 4.　Percent Hydrocarbon Composition (ppb) of E10 Gasoline Headspace Vapors[30]

Ethanol	Paraffins	Olefins	Aromatics	Unknowns	Fused Rings
6.4	57.7	12.2	18.3	2.5	0.2

Fluoropolymers are a specific class of polymers which are well suited for fuel permeation resistance due to the combination of attributes they exhibit. The high polarity of the carbon-fluorine bond gives fluoropolymers low surface energy and discourages the absorption of most solvent vapors. Fluoropolymers are also semi-crystalline polymers and form dense crystalline structures, which is attributed to the relatively short C-F bond length and relatively small Van der Waals radius of the fluorine atom. For example, polytetrafluoroethylene (PTFE) exhibits a higher degree of crystallinity (60-80%) than that of polyamide 6 (35-45%) while also displaying a higher crystalline density ($2.35g/cm^3$) than that of high density polyethylenes ($1.00g/cm^3$)[31]. The strength of the C-F bond also provides high chemical stability and flame resistance which are important considerations for fuel containment.

Homogeneous Materials

A homogeneous material which economically provides low fuel permeability with adequate durability and flame resistance represents the optimal material for molded polymer fuel tanks. Many non-fluoropolymer candidate materials which display low fuel permeability are polar, crystalline polymers which typically exhibit low impact strength, especially at low temperatures, and must be modified to realize adequate durability. Of the polyamides, high-carbon grades such as polyamide 11 and 12 are inherently more durable than polyamide 6 and provide similar permeation resistance. This advantage is offset by higher material costs and a more limited supply chain. Both polyamide 11 and 12 are commercially available for rotational molding. Several fluoropolymers, namely polyvinylidene fluoride (PVDF), ethylene-tetrafluoroethylene (ETFE), and perfluoroalkoxy alkane (PFA) have been demonstrated and commercialized for use in rotational molding; however, the high melt temperatures of ETFE (~260°C) and PFA (~300°C) discourage their use in fuel tank applications and are used primarily to create thin-wall linings for metallic components[32].

Polyamides 11 and 12

Polyamide 11 is produced through polycondensation of 11-aminoundecanoic acid, a fatty acid with amine end functionality which is derived from castor oil. Polyamide 12 is derived from petroleum sources and is polymerized through the ring opening of laurolactam, a cyclic amide. The melt range of polyamide 11 is between 180 and 189°C with polyamide 12 melting at approximately 10°C lower. The glass transition temperature for both polymers is approximately 40-45°C[33]. Polyamide 11 has been evaluated under the ARM impact test method with a reported failure energy of 65J at room temperature[34]. Both materials exhibit good solvent resistance to petroleum products, although swelling in seen in the presence of ethanol, especially at elevated temperatures[35]. Polyamide 11 has been utilized in low-permeability, multi-layer strategies which meet CARB permeation requirements but its performance as a single-layer solution has not been publicly evaluated. Polyamide 12 has long been used by the

automotive industry as a fuel line material but is also used in multi-layer architectures to supplement permeation performance. Additionally, it is not recommended that nylon 12 be directly in contact with fuel sources, as it has been shown that ethanol-based fuels are capable of dissolving its constituent materials (i.e. plasticizer, monomer, and oligomer)[36].

Polyvinylidene Fluoride

PVDF is produced through free-radical polymerization of vinylidene fluoride using either emulsion or suspension methods. Its precursor, vinylidene fluoride (VDF), is an unsaturated fluorocarbon derived through various mechanisms from fluoro- and chloro-carbons[37]. PVDF exhibits an initial melt temperature of approximately 160°C and can be heated up to 300°C, enabling it to be processed in a number of methods[38]. PVDF possesses many beneficial attributes, especially when viewed as a fuel containment system, including: high mechanical strength and toughness, high thermal stability, high solvent resistance, and UV stability. Furthermore, PVDF requires oxygen-rich environments to burn and has been given UL94 V-0 classification under the UL vertical burn test[39]. The glass transition temperature of PVDF is approximately -40°C.

Copolymerization of PVDF with other fluoropolymer species allows for the enhancement of material properties. For example, copolymers constructed from VDF and tri- or tetra-fluoroethylene (TFE) exhibit increased crystallinity and are utilized to realize higher strength and stiffness. The copolymerization of VDF with hexafluoropropylene (HFP) has the opposite effect, reducing the overall crystallinity to realize gains in ductility and impact performance[40]. VDF-HFP copolymers have demonstrated high impact strength at room temperature, with *No Break* conditions reported for unnotched and notched Izod specimens[38]. Two commercially-available fluoro-terpolymers, THV (TFE-HFP-VDF) and HTE (TFE-HFP-PE) also exhibit similar melt temperatures to that of PVDF and have demonstrated *No Break* Izod impact performance in notched specimens tested at -40°C[41].

The fuel permeation performance of PVDF and PVDF copolymers has been investigated in extruded polymer fuel lines. Fuel lines having approximately 0.4mm wall thickness were exposed to fuels, including CE10, and soaked at 40˚C. A mass-loss determination resulted in CE10 fuel permeation rates ranging from 1.8 g/m²day in PVDF homopolymer to 2.2 g/m²day in a copolymer grade. The permeation rates were approximately an order of magnitude less when a non-ethanol fuel was used[42]. Although the observed permeation rates do not meet or exceed the required CARB/EPA limits, it is likely that an increase in the barrier thickness will further limit the permeation rate, as polymeric fuel tanks typically require 4-5mm nominal wall thickness for adequate strength and stiffness. However, a balance must be reached between the performance requirements and the cost of the overall article, as the relative material cost of PVDF in comparison to HDPE is approximately ten-fold[43]. PVDF has been commercialized for use in rotational molding by Arkema under the trade name of *Kynar* homo- and co-polymers.

Alloys, Blends, or Reinforced Systems

Attempts have been made at formulating durable, fuel-resistant polymers by altering the base composition of homopolymers. Polyamides are inherently resistant to hydrocarbons, but are susceptible to the ingress of polar solvents such as ethanol, and typically possess poor impact strength, especially at subambient temperatures. A number of commercially available, impact-modified polyamide systems exist; however, their suitability in rotational molding is not well understood. Alternatively, attempts have been made to increase the fuel permeation resistance of highly durable polymers. The barrier properties of polyethylene may be enhanced by the intercalation of fuel-resistant species within the polymer structure. Such systems have been experimentally demonstrated in rotational molding but have not reached full commercialization.

Impact-Modified Polyamides

Several strategies exist for toughening polyamides, but their use in rotational molding and ability to maintain high permeation resistance requires further consideration. One impact-

modified nylon specifically formulated for commercial use in rotational molding has received

CARB certification for fuel permeation of small off-road engine components. Custom Resins'

494-IM nylon system has received executive order Q-13-016 and has met the fuel permeation

requirements under TP-901 using CE10 test fuel and a tank geometry with 3.0/3.7mm

minimum/nominal wall thicknesses[44]. According to its published technical data sheet, 494-IM

possess a melt temperature of 218˚C and exhibits high impact properties in accordance with the

ARM Low-Temperature Impact Method, with 135J reported at -20˚C and 108J at -40˚C[45]. The

data sheet also includes a recommendation to process the material in the presence of an inert

gas in order to minimize thermal oxidation – a strategy which was likely employed to reach the

published impact energies.

    Impact modification strategies for polyamides can be broadly classified as modified-

olefin, modified-rubber, modified-styrenic, or ionomer types. The appropriateness of each

method should be determined by considering the likely effect each will have on the low-

temperature impact and fuel permeability of the polyamide system, as well as how likely the

impact-modified phase can withstand the aggressive thermal environment seen during molding.

With each strategy it is assumed the impact-modified phase is melt compounded into the

polyamide prior to the generation of ground particles in order to gain sufficient dispersion of the

modified phase within the polyamide.

    Modified-olefin systems for polyamides impart the beneficial aspects of polyolefin

materials, primarily low-temperature impact, through chain interaction. These modifiers are

created by functionalizing polyolefin chains, typically through the grafting of a reactive species

such as an acid anhydride. The anhydride group imparts polarity to the molecule, increasing its

attraction to the polyamide matrix, and may participate in bonding through reactions with the

amine end groups of the polyamide. A commercial example of a modified-olefin system

designed for use in polyamides in Dupont's *Fusabond N493* impact modifier. Fusabond N493 is

a modified ethylene-octene copolymer grafted with 0.5% maleic anhydride content[46]. In

notched Izod impact testing of injection molding specimens, Fusabond N493 was found capable of increasing both the ambient and subambient impact performance of polyamide 6 with strong correlation to the weight loading of the modifier. At a 10% weight loading, an approximate 400% increase in impact strength has been demonstrated at room temperature, with an approximate 75% increase at -40°C. A higher weight loading of 20% Fusabond N493 is capable of increasing the room temperature impact 1100% whereas the -40°C impact improves nearly 100%[47]. Although impact performance may be greatly enhanced by the incorporation of a modified-olefin system at high weight loadings, other material properties may be negatively affected, namely the strength, stiffness, heat resistance, and viscosity of the polyamide. Polyethylene undergoes thermal and thermo-oxidative degradation at temperatures exceeding 200°C, with branching and crosslinking occurring in the approximate range of 225-250°C[48]. Rotational molding grades of polyamide 6 has been found to achieve sufficient void dissolution at a peak internal air temperature of approximately 240°C; however, technical literature for Fusabond N493 provides that it may experience a maximum processing temperature of 290°C[49]. The incorporation of a polyolefin modifier will likely reduce the overall fuel permeability of a polyamide system as polyolefins are fuel-permeable and their inclusion with the polyamide interrupts its crystalline structure.

Modified-rubber systems are analogous to the polyolefin systems but instead attempt to incorporate functionalized elastomers within the bulk polyamide. Modified ethylene-propylene rubber (EPR) and ethylene-propylene-diene-monomer rubbers (EPDM) are both commercially available for incorporation in polyamide systems, with Fusabond N416 (EPR) and Royaltuf 498 (EPDM) serving as examples. Both systems provide comparable performance to modified-olefin systems when added at sufficiently high weight loadings (10-20%) but exhibit additional concerns in regards to thermal oxidation and chemical resistance[50]. Experimental work has found that thermal oxidation begins in these materials between 150 and 200°C, with EPDM possessing significant vulnerability due to its unsaturation[51]. Additionally, both rubbers exhibit

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poor resistance to petroleum-based products, and swelling is observed under exposure to gasoline.

Modified-styrenic systems consist of grafted styrenic compounds such as styrene-ethylene-butylene-styrene (SEBS) triblock copolymers. SEBS-based impact modifiers are commercially available through the Kraton Corporation as *Kraton G* and *Kraton FG* products, where Kraton G are non-functionalized copolymers and Kraton FG are functionalized with succinic anhydride. SEBS modifiers are similar to polyolefin modifiers in that the rubbery component responsible for low-temperature impact is a fully saturated olefin which allows for increased temperature resistance during processing. Polyamide/SEBS blends have achieved increased low-temperature impact strength at high weight loadings (20%) by incorporating differing amounts of functionalized and non-functionalized modifiers. For example, the low-temperature (-29°C) notched-Izod impact strength of a polyamide/SEBS blend was found to increase 500% when a 20% weight loading of SEBS was incorporated in which the SEBS phase consisted of 4% functionalized SEBS and 16% non-functionalized SEBS[52]. SEBS is not recommended for exposure to gasoline and other hydrocarbons due to swelling and softening.

Ionomers are copolymers which contain both neutral-charge and ionized repeating units. A commercial example, Dupont's *Surlyn* brand of ionomers, is an ethylene-methacrylic acid copolymer in which sodium cations are used to neutralize a portion of the acid groups. The presence of the acid group imparts polarity in the overall polymer and reduces crystallinity by interrupting the ethylene network, and the presence of ionic bonding provides increased strength and toughness. Ionomers are also capable of being highly tailored, as the relative number of repeating units, the ion species, as well as the amount of acid neutralization can all be manipulated. Ionomers are suitable for impact modification in polyamide systems as the amine or acid end functionalities of the polyamide chains are capable of interaction with the ionized functional groups in the ionomer[53]. Ionomer-modified polyamide 6 blends were evaluated in rotational molding as early as the 1980s by Allied-Signal. In United States Patent 4,970,045 it is

reported that a grade of Surlyn using zinc as the neutralization species was capable of achieving exceptional room temperature ARM impact energy (224J) in 1/8" thick molded articles when included at a 5% weight loading. Compared to unmodified polyamide 6, the ionomer blend also nearly doubled the -40°C impact energy, increasing it from 25J to 68J[54]. Ionomer species such as Surlyn possess good barrier performance and are commonly used in food packaging systems due to their high optical clarity and ability to form thin films. Ionomers are compatible with gasoline and other petroleum products; however, alcohols have been identified as stress-crack promoters[55] and their use in fuel containment is not well demonstrated.

In summary, there exist many impact-modified polyamide systems which have demonstrated increased impact resistance at ambient and subambient temperatures. Of the strategies which employ chemically-modified molecules to achieve good dispersion and reaction with the polyamide phase, most require high weight loadings (10-20% by weight) to realize modest to excellent gains in impact strength at low-temperature. At these weight loadings the mechanical strength of the polyamide is likely to be compromised, as well as its overall permeation resistance. Ionomer-type modifiers show better promise as they have been demonstrated in rotational molding and see commercial use in existing barrier applications; however, the ability of alcohols to promote stress-cracking is of concern for fuel tank applications.

Intercalation

Another strategy for increasing the barrier properties of a polymer system is to introduce intercalated materials which disrupt pathways through the polymer and thereby slow the overall rate of permeation. Nanocomposite systems, primarily nanoclays, are capable of slowing gasoline permeation provide that they become well-dispersed inside a polymer matrix. The low-shear environment of rotational molding is largely incapable of dispersing fillers at the macro scale and so nano-material inclusion must be performed through melt compounding of the base resin.

The addition of nanoparticles typically results in an increase in melt viscosity of a polymer. This is problematic in rotational molding as the melt viscosity is the primary driver in the dissolution of air bubbles generated during polymer sintering. Therefore, processing conditions must be altered to produce articles of sound mechanical structure. Some work has been performed in nanoclay dispersal in which the melt viscosity is only slightly altered[56,57]. This is typically achieved by treating the surface of the nanoclay and utilizing modified polymer species which aid in achieving high levels of dispersion[58]. The presence of nanoclay materials may also reduce the impact resistance of polymer systems, and so the loading must be optimized to arrive at high barrier properties without sacrificing material performance.

At the current time, no commercially available system exists for rotational molding polymers containing intercalated barrier species. Blow molders, however, can produce articles made from a novel intercalated system designed for fuel applications which combines standard blow-molding grades of polyethylene with an additive of nanoclay-reinforced polyamide. This system is advantageous as it is incorporated at the melt screw just prior to blow-forming; however, a more stringent and unforgiving processing window is also observed. For sufficiently high additive loadings in sufficiently thick materials, gasoline permeation levels below CARB and EPA requirements have been demonstrated[59].

Post-Molding Treatments

Post-molding treatments can be used to enhance the permeation performance of a molded article. These processes are advantageous for the rotational molder because they do not extend the cycle time of the molding operation or add processing complexity. In contrast, additional capital equipment is needed to realize these strategies, which may or may not be performed by the rotational molder.

Fluorination

The ability of polyethylene to participate in a fluorine-hydrogen exchange reaction in the presence of diatomic fluorine gas provides a useful mechanism by which to increase the barrier

properties of a fuel container. The gasoline permeability of fluorinated polyethylene has been

demonstrated to meet and exceed both CARB and EPA permeation limits, with one commercial

system offering permeation rates of less than 0.5g/m²/day[60]. The fluorination process

improves gasoline permeation through three different mechanisms, by reducing the free volume

within the polymer structure, by causing crosslinking within the structure, and by changing the

surface energy and polarity of the surface[61].

     Fluorination is an attractive process for the rotational molder because it allows for the

widespread production of polyethylene articles. The processing of polyethylene is well-

understood in rotational molding and numerous formulations exist which are inexpensive and

specifically tailored for the process. However, several distinct disadvantages are present when

considering fluorination. The toxicity and reactivity of fluorine gas poses a significant safety risk

and the treatment must be performed in a well-controlled environment.   The cleanliness of the

articles to be treated must be closely monitored, as residual water will react to produce

hydrofluoric acid, and contaminants may participate in highly exothermic reactions which

destroy the container itself. Fluorination is most efficiently performed in large, heated

containers where multiple tanks can be exposed to a single gas stream. This causes both the

interior and exterior of the fuel containers to be treated which may result in undesirable effects

to the aesthetic appeal of the article, including reduced surface gloss and discoloration of

applied decals. The fluorination treatment may also not be compatible with additional polymer,

elastomer, and metallic components typically used in fuel tank constructions. Therefore,

grommets, fuel pickups, vents, and caps are typically installed post-treatment.   Additionally,

the exact cost of fluorinating rotationally-molded articles is not well understood. In comparison

to the cycle time of rotational molding (~20min.), it is believed that the fluorination treatment

time far exceeds this amount, perhaps even by an order of magnitude. Also, because the

treatment is not performed in-process, one must account for the additional labor, handling,

space, and capital equipment needed.

Epoxy Coatings

Thermosetting polymers such as epoxies are capable of exhibiting high barrier performance due to their ability to incorporate and disperse intercalated barrier materials such as nanoclays and silicates. Such materials are incorporated via surface treatment and high-shear or sonication methods into the uncured resin prior to the addition of the hardening agent and remain in the structure as the polymer network is formed.

The incorporation of a high-barrier epoxy coating into a rotationally-molded article can be achieved by introducing the epoxy after the solidification of the polymer article. A uniform layer can be deposited within the article provided that the reacted epoxy has appropriate viscosity and bi-axial rotation is maintained. In this regard, the application of the epoxy coating can occur in secondary machinery that need not necessarily incorporate the molds from which the articles were formed.

Additional considerations are needed for incorporating epoxy coatings within rotationally molded articles. The selection of the primary material, as well as its compatibility and adhesion with the epoxy must be understood. Polyethylene is a likely choice for such systems but exhibits poor interaction with epoxy. It may be possible to augment the interfacial interaction by oxidizing the inner surface of the polyethylene, incorporating a compatabilizing species which selectively melts and distributes at the part interior, or by using a crosslinked polyethylene which deposits crosslinking residuals at the inner surface. The durability of the epoxy coating must also be considered, as it resides at the inner surface and experiences high loadings under impact. Rubber-toughening of epoxy has been demonstrated under a variety of techniques, typically by incorporating a liquid rubber such as C- or A-TBN (carboxyl or amine-terminated butadiene-acrylonitrile)[62,63] or a rubber latex such as styrene-butadiene rubber (SBR)[64].

A low-permeation epoxy system has been commercialized by the Mitsubishi Gas Chemical Co. under the trade name *Maxive*. Promotional literature provides that it is a

polyamine-cured epoxy which is compatible with polyolefin materials, and exhibits fuel permeation rates of 0.05 g-mm/m^2-day[65].

Summary of Single-Layer Strategies

Single-layer strategies for low-fuel permeation are sought by rotational molders for their ease of implementation. Fluoropolymers provide low-fuel permeation while maintaining acceptable durability, albeit at greater expense. Polyamide materials exhibit good fuel permeation but must be impact modified to realize adequate durability, especially at low temperature. Many of the impact modification strategies used in polyamide systems must be added at high weight loadings to realize adequate performance, and the resulting effect on fuel permeation performance must be understood. Intercalating a durable polymer such as polyethylene is likely to improve its barrier performance, although this strategy has yet to reach commercial viability for rotational molders.

Post-mold treatments are also attractive for the rotational molder as it allows them to achieve high permeation performance while processing simple, low-cost materials such as polyethylene. Fluorination has been found highly effective in increasing gasoline permeation in polyethylene but poses significant safety, logistical, and procedural challenges for the rotational molder. The incorporation of a high-barrier epoxy coating on the internal surface of molded articles may provide exceptional permeation performance provided that the epoxy system can adhere to the molded article and possess acceptable durability.

CHAPTER 3. MULTI-LAYER ARCHITECTURES

Although attempts have been made to develop single-layer systems by increasing the barrier properties of polyethylene or by increasing the impact strength of polyamides, the use of multi-layer, multiple material systems allow molders to overcome single-layer deficiencies. The rotational molding process provides access to tooling while the polymer is still in the molten state, thereby enabling the reintroduction of additional materials. This is done either by manual introduction through an open port or vent in the tool, or by encasing the secondary material in a container residing on the exterior or within the tool. Vent openings are present in each mold which extend through the mold wall and into the hollow interior, and allow for the removal of expanding gasses during heat-up as well as the introduction of ambient air during cooling. Vents are typically constructed of low surface energy, temperature-resistant polymers such as PTFE or polyether ether ketone (PEEK) which do not allow materials to melt and adhere during heat up. Removing the vent or a similarly designed plug allows for access to the part interior after outer layers have been deposited. Manual servicing of a mold is convenient as it requires no additional technology or equipment, but adds time to the process cycle as the mold must be removed and reintroduced back into the oven, and poses a significant safety risk caused by contact exposure to high surface temperatures.

One common strategy used to create multi-layer construction is by employing an insulated *drop box* which is charged with the secondary material and mounted to the mold exterior. The drop box is pneumatically activated, and air supplied through the primary drive arm of the molding machine activates the dropping of the secondary material into the mold interior at a programmed set point. The drop box method is preferred for its efficiency but requires additional mold construction and machine functionality to execute. Novel systems to create multi-layered articles using a single material introduction will be discussed in Chapter 4.

Commercially Demonstrated Architectures

Current multi-layer schemes utilize polymers having complementary properties to achieve high performance. Popular examples of such schemes include dual-layer polyethylene/polyamide (PE/PA), and triple-layer polyethylene/ethylene vinyl alcohol/polyethylene (PE/EVOH/PE). Each system has been demonstrated commercially and has received a CARB executive order for meeting fuel permeability requirements.

PE/PA Dual Layer

Dual-wall PE/PA formulations are advantageous in that they require a single secondary introduction and thus minimize the time required to service a tool. However, a large disparity exists between the melting temperatures of polyethylene and polyamide, and so process characterization and an understanding of mold-to-mold heating variation is required. This disparity in melt temperature is problematic as it requires that the polyethylene be sufficiently protected from thermal oxidation as the temperatures required for polyamide melting are reached. Furthermore, the lack of affinity between polyethylene and polyamide typically requires that an additional species be present in the melt to achieve optimal mechanical performance of the tank construction and to prevent delamination of the adjacent layers.

WO Patent 2004045849 A1 describes multilayer rotational molding using different combinations of polyolefin and non-polyolefin layers, including polyamides and fluoropolymers. Development of the technology was conducted as a collaboration between Total Petrochemicals and Arkema Inc., developers of the polyolefin and polyamide systems, respectively. The described technology involves utilizing functionalized or grafted polyolefins in to achieve adhesion to a polyamide interior layer. Ideally, this is performed by employing anhydride-grafted polyolefins in the presence of a diamine polyamide, in which the polyamide exhibits end functionality which has been manipulated to have a high amine content. The goal of this specific formulation is to create amide linkages between the anhydride and amine functional groups, providing covalent bonding between the dissimilar materials[66].

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US Patent Application 20080203623A1 describes the design of a rotationally molded fuel tank comprised of a polyethylene/polyamide dual-layer construction or of a polyethylene/polyamide/fluoropolymer tri-layer construction, a technology developed by the Honda Motor Company. This technology discloses that 'a polyamide resin as low as possible in melting point is selected', to minimize the disparity between the polyamide and polyethylene melting temperatures. Long carbon-chain polyamides (e.g. PA11 and PA12) are recommended for multi-layer constructions, as their low melt point facilitates the buildup of a barrier layer (<0.100") in an efficient timeframe without causing excessive thermal oxidation of the polyolefin outer layer. However; the barrier properties of such long-chain polyamides may be insufficient, and so a tri-layer construction utilizing a fluoropolymer interior layer, is recommended. In this construction, the polyamide layer functions as an intermediate tie layer as it possesses better adhesion to each material in comparison to a direct polyolefin/fluoropolymer interface[67].

In sum, rotationally molded polyethylene/polyamide dual-layer systems have been demonstrated in a variety of different processing methods. However, it is noted that such systems achieve optimal success upon careful selection of the polyamide species, whether to achieve affinity with the polyethylene layer or to most closely match its melting point. Also, the presence of a third species, a compatibilizing agent, is recommended to promote layer-to-layer interaction and prevent delamination.

XLPE/EVOH/XLPE Triple Layer

One popular commercial system for rotational molding of low-permeation fuel tanks is Centro Incorporated's RotoLoPerm triple layer system. The technology was patented in late 2013 and received both CARB and EPA low permeation certifications in 2006 and 2009, respectively. RotoLoPerm uses an EVOH barrier layer to resist vapor permeation, and encases the layer between inner and outer layers of cross-linked high-density polyethylene (XLPE) to realize high impact performance. US 8,597,747 provides that the technology was developed as an alternative to polyamide/polyethylene dual-layer systems, namely those utilizing polyamide

11, as "Polyamide 11 lacks low temperature dart impact strength. . .(and) the cost of Polyamide 11 may also be a limiting factor."[68] According to CARB Executive Order Q-08-027A, the RotoLoPerm system achieves the required permeation rate provided that the average barrier-layer thickness is no less than 0.5mm and that the average overall wall thickness of the container is no less than 2.5mm[69].

Ethylene-vinyl alcohol (EVOH) copolymers are a popular choice when considering the design of a container requiring low vapor permeation performance; however, their use in the rotational molding process requires certain considerations. The relative ethylene/vinyl alcohol content dictates both the permeation performance as well as the melt temperature of the bulk material, with relatively higher alcohol content formulations having better permeation performance and a higher melt temperature. The glass transition temperature of EVOH materials is typically found in the range of 40-80°C, and so the barrier layer suffers poor durability under impact loads at ambient and sub-ambient temperatures. The polyethylene provides both an inner and outer protective layer, absorbing impact loads while preserving the barrier performance of an unfractured EVOH layer. The choice of a cross-linkable polymer is also deliberate, as the inclusion of cross-linking reagents improves its adhesion to EVOH. XLPE is widely used in rotational molding due to several important attributes: high environmental stress cracking resistance, relatively high creep resistance, UV stability, and good ductility under loading or pressurization. Furthermore, ground XLPE can be purchased at commodity prices and its processing in rotational molding is well understood.

Processing of a XLPE/EVOH/XLPE triple layer system is typically carried out by removing a heated mold from the oven and manually adding the second and third materials through an open port. Most critical is the time at which the innermost layer is added to the mold. This layer of XLPE absorbs most of the stress under an impact load, and so this layer must be sufficiently thick, uniform in its distribution, and be largely unmixed from the EVOH to avoid large-scale stress transfer and/or fracture of the EVOH. Slight mixing of the layers is

encouraged to promote adhesion, however, and so it is advised that the deposited material reach a prescribed temperature before each successive material is introduced. Failing to do so could result in delamination upon cooling or under applied stresses. The use of 'adhesive agents' such as grafted polyolefins, modified ethylene vinyl acetate, ethylene methyl acrylate, or other grafted polymers have been demonstrated as effective in improving interfacial adhesion. Such reagents can be dry blended or compounded into the polyethylene prior to molding, or added to the mold as a distinct 'shot' just prior to adding the second and third materials[68].

Considerations for XLPE/Fluoropolymer Articles

It is desirable that a bi-layer article composed of a polyethylene outer-layer and a fluoropolymer, such as PVDF, inner-layer be molded for the purpose of fuel containment. Such a system should realize a greater ease of processing in comparison to tri-layer strategies, and should also deliver greater barrier performance and overall part durability in comparison to polyethylene/polyamide articles. The use of polyethylene for the outer layer is maintained in all scenarios as it provides both UV stability and good aesthetic appeal with the ability to incorporate in-mold decals. Crosslinked polyethylene is favored over medium or high-density polyethylene in this application given its ability to contribute crosslinking reagents to the system which may augment interfacial adhesion. The crosslinking of polyethylene is a heat activated process which occurs during molding, ideally after the melt sintering has been completed as the crosslinking process increases melt viscosity and discourages gas dissolution thereafter. The crosslinking is accomplished through peroxide decomposition and the generation of free radicals. Coagents are also used to generate more highly-active radical species which carry out the crosslinking process more efficiently. Dicumyl peroxide or alkyl-substituted peroxy-hexynes are typically used as the peroxide species, whereas triallyl cyanurate or triallyl isocyanurate serve as the coagent. Both peroxide and coagent are added at less than 1.0% by weight[70,71].

The lack of affinity between PE and fluoropolymers in general presents a challenge which must be overcome in order to realize articles which do not delaminate while in-service,

compromising its mechanical integrity and permeation performance. The interfacial compatibility of polyethylene/fluoropolymer systems has been studied in a variety of applications and some may be appropriate for use in rotational molding. It is preferred that the interfacial adhesion be considered either through additives or surface treatment of either polymer phase which is performed prior to molding. Chemical etching may also be used to improve the surface adhesion of fluoropolymers but does not appear to be well-suited for the present application as it likely requires additional processing time and poses an inherent safety risk.

The use of an intermediate tie layer has been shown to increase the peel strength of compression molded PE/PVDF+HFP plaques. In this investigation the optimal tie layer weight composition was found to be 65% of an aliphatic polyester-based polyurethane thermoplastic elastomer mixed with 35% of a maleic-anhydride grafted polyethylene, and the ratio of tie layer to integral layer thickness was approximately 1:3[72]. The use of melt-compression in this application was likely to have influenced the bonding strength of the tie layer to the integral layers. This effect cannot be replicated to the same degree in rotational molding, however, tie layers should be added before the outer layer reaches solidification in order to maximize chemical bonding and mechanical interlocking. In-mold pressurization may also facilitate greater interfacial bonding if applied after all layers have been established but are still above the solidification temperature.

High-adhesion grades of fluoropolymers have been developed for use as tie-layer compounds in extruded applications and their use in rotational molding requires consideration. Examples include DuPont/Chemours *Tefzel* HT2202 ETFE and Daikin *Neoflon* RP-4000 Series EFEP copolymers (ethylene+fluorinated ethylene propylene). The ethylene composition of these materials provides reactive sites in which grafting can be used to substitute a compatabilizing species such as an acid anhydride while maintaining the overall fluoropolymer character of the molecule. EFEP compounds are more suitable for use in rotational molding as

their melt temperature is approximately 160˚C whereas ETFE-derived materials exhibit a melt temperature of approximately 265˚C[73,74]. In the proposed XLPE/PVDF bi-layer system processing temperatures must be driven to approximately 200˚C to achieve adequate crosslinking throughout the XLPE outer layer, and the melt temperature of the PVDF inner layer is also approximately 160˚C. It is likely that an EFEP tie-layer species could be added to the bulk XLPE powder and develop a distinct, separate layer provided that its particle size is sufficiently larger than that of the XLPE powder.

Surface treatments have been used to enhance the interfacial properties of both polyethylene and fluoropolymer systems. Corona discharge, flame, and plasma treatment methods can all be used to modify surface energy of polymers; however, methods which are capable of treating ground particles are of particular interest in the application of resins for rotational molding. Low-pressure air (atmosphere) plasma treatment is capable of imparting functionality onto polymer powders and is the preferred method of surface treatment for powders given its relative cost and efficiency. Air plasma treatment has been successfully demonstrated in PVDF thin films and was found capable of reducing the contact angle of water/PVDF interfaces by approximately 40% after 20 minutes of treatment[75]. For the present application it is desirable for plasma-treated PVDF powders to be dry blended into the bulk PVDF powder just prior to introduction into the mold.

One-Shot Processing Methods for Multi-Layer Articles

Proprietors of multi-layer systems have devised novel methods by which to most efficiently achieve these constructions. Such 'one-shot' systems are advantageous because they require only one introduction of material into the mold and do so without the use of additional equipment.

Sequential Sintering of Mixed Materials

One such method is to directly blend two dissimilar materials having a sufficiently large disparity in melt temperature and particle size. The material having the lowest melt

temperature should be ground into the smallest particle size so that it preferentially melts first to the mold interior. The second material requires more time and a higher developed temperature to achieve melt and is therefore deposited on top of the first material which has become fully sintered to the mold wall. This technique is described in WO2004/045849 where suggested disparities between the particle size and melt temperature of the different layers are provided. In the provided example a PE/PA or PE/PVDF bi-layer system is investigated. In regards to melt temperature it is suggested that the polyethylene system exhibit melt temperature '...at least 15°C lower than that of the PA or PVDF'. The input particle size ratio of PE to PA or PVDF is recommended to be no greater than 0.5, with the PE material typically consisting of a ground particle (100-1500μm) and the PA or PVDF material being comprised of either micropellets (200-1500μm) or pellets (2-4mm)[76].

The above technique is believed to be well-suited for the proposed XLPE/PVDF bi-layer candidate system described previously. In regards to melt temperature, high density polyethylene possesses a melt temperature of approximately 130°C whereas the PVDF and EFEP tie-layer materials possess a melt temperature of approximately 160°C. XLPE resins for rotational molding exist primarily as ground powders at 20-35 mesh size whereas both PVDF and EFEP tie-layer materials are provided in pellet form. It is likely that the pellet size of the fluoropolymer components is excessively large and will require considerable heating time to achieve full consolidation. A micropellet form represents a more optimal configuration in which processing time and heat exposure is minimized; however, the excellent heat stability of the XLPE outer layer allows it to process under high residence times without the observance of deleterious effects.

Material Release via Sacrificial Film Bagging

Another demonstrated one-shot system involves encasing the inner layer material in a sealed bag constructed from polymer film. The film is chosen from a material possessing an intermediate melt temperature, greater than that of the outer layer but less than that of the

inner layer. The outer layer is first deposited before the bag material experiences melt, releasing the inner layer material. The polymer film material must be carefully chosen, however, as it must exhibit compatibility with each material to avoid contributing detrimental effects to the overall part construction. US Patent 8029718 B2 describes a process for forming multi-layer molded articles predominantly of various polyethylene/polyamide constructions. This technology was developed by Arkema Inc., and later commercialized as their PetroSeal material system. A one-shot material system is described in which the interior polyamide feedstock is enclosed is a polymer film bag and introduced into a mold along with a charge of polyethylene powder. The bag construction is carefully chosen by considering its material composition and functionality, melt viscosity, and toughness/tear resistance, as well as the film thickness of formed bag. Reduced barrier and mechanical performance in the overall container are observed if the bagging construction allows for premature mixing of the outer/inner layer, or suffers from a delayed melt in which it becomes entrapped within the inner layer[77].

In the conducted trials it was found that the melt temperature of the bagging should be selected so that it is at least 20˚C greater than that of the outer layer and 20˚C less than that of the inner layer. Optimal layer separation was achieved in PE/PA 11 systems when the bagging material used exhibited an intermediate melt temperature that was approximately 35˚C greater/less than that of the integral layers. A co-polyamide release film was selected as the optimal bagging material given its melt temperature and compatibility with the PA 11 inner layer[12]. For the proposed XLPE/PVDF bi-layer system the proximity of melt temperatures restricts the selection of the bagging material under these stipulations. However, the trials conducted in the PE/PA 11 system did not test a bagging film that had a melt temperature comparable to that of the inner layer. Bagging films with melt temperatures comparable or equivalent to that of the outer layer resulted in large-scale intermixing of the powders, but those with melt temperature comparable to the inner layer were not examined. As PVDF films are commonplace it is believed that a PVDF bag construction would be well-suited for the intended

application. In the ideal case the bagging material would be produced from commercially available flexible PVDF copolymer systems which possess an intermediate melt temperature (145°C) between that of XLPE and PVDF, such as *Kynar Flex 2800*[78].

CHAPTER 4. CONCLUSION

The process of rotational molding is well-suited for the production of fuel containers which comply with established fuel evaporative emission requirements. Containers made from a single polymer species are unlikely to possess high fuel permeation resistance while exhibiting adequate durability. Polyamides have been traditionally utilized for their high fuel permeation resistance, but are limited by poor impact performance at sub-ambient temperatures. Through the process of fluorination, the fuel permeation of polyethylene is enhanced while high impact strength is maintained. This process possesses significant health and safety risks, however, and requires added post-processing time and cost. Incorporating high-barrier, intercalated materials is likely to reduce fuel permeation when added to the polymer or as part of an epoxy coating applied as a post-process, although neither strategy has reached commercial viability.

Multi-layer processing allows the molder to realize the attributes of multiple material systems. Typically, a material with high fuel permeation resistance is paired with one exhibiting high impact strength. Material selection and process conditions must be scrutinized in order to create molded articles with sufficient interfacial adhesion and impact performance. The direct introduction of secondary materials increases process complexity and affects throughput.

Through the use of certain technologies, multi-layer architectures can be formed through a single material introduction. These methods streamline production, reduce processing variability, and eliminate a point of defect introduction. Two distinct materials may sequentially sinter in the melting phase provided that their melt temperatures and particle size are appreciably different. To create a well-defined interface, a sacrificial release film should be used to contain the inner layer material until the outer layer has been deposited. It is believed that a multi-layer architecture comprised of a cross-linked polyethylene outer layer and polyvinylidene fluoride inner layer represents an optimal container construction which provides the greatest number of beneficial attributes: low fuel permeation, high durability, elevated temperature and flame resistance, visual appeal, and competitive cost.

In the creation of a XLPE/PVDF bi-layer system, it is critical that strong interfacial adhesion exist. Future work should focus on examining different aspects which improve polyethylene/fluoropolymer adhesion in the context of rotational molding. For example, plasma-treated PVDF resin is likely to increase compatibility, but determining the critical loading level and whether or not the surface treatment alters the consolidation process is of primary interest. Also, the use of commercially-available fluoropolymer tie layer compounds requires further investigation. Modified ETFE compounds exhibit a melt point comparable to that of PVDF and of interest is whether or not they may be introduced into the mold along with the PVDF and impart a compatibilization effect.

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APPENDIX

Association of Rotational Molders International
Low Temperature Impact Test

Version 4.0 - July 2003

Appendix F *(continued)*
Sample Forms – Ft.-Lbs.

Laboratory: __ABC Company__ Operator: __John Doe__ Date: __January 1, 2000__

Sample: __B__ Material Type: _____ Source: _____

Manufacturer's Code: _____ Processing History, Temperature, Cycle Time, etc.: _____

Additional Information: _____

O denotes non-failure
X denotes failure – ductile
✳ denotes failure – brittle

Check one: O Procedure A - 10 lb. (4.536 kg)
✗ Procedure B - 15 lb. (6.804 kg)
O Procedure C - 20 lb. (9.072 kg)
O Procedure D - 30 lb (13.61 kg)

Drop Height	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20				n_j	i	in_j
8																										
7.5						✳																				
7	X		X		O		X										X							1	3	3
6.5		O		O				X		X			X			O		X						3	2	6
6									O		X	O		X	O				O					4	1	4
5.5												O			O									2	0	0
																						Total =	10		13

$h = h_0 + [\Delta h (A/N \pm 0.5)]$ $N =$ __10__ $A =$ __13__   Sample Calculation w/ 15 lb. dart and non-failures as events:

$MFE = h \times w$ (for ft.-lbs.) $h = 5.5 + [0.5 (13/10 + 0.5)] = 6.4$ ft.

$MFE = h \times w \times g$ (for J) $h_0 =$ __5.5__ $\Delta h =$ __0.5__ $MFE = 6.4$ ft. $\times$ 15 lbs. $= 96$ ft.-lbs. $MFE =$ __96 ft.-lbs.__

Figure A1.   Sample ARM Low-Temperature Impact Test Sheet