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A liquid xenon ionization chamber in an all-fluoropolymer vessel

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Abstract

A novel technique has been developed to build vessels for liquid xenon ionization detectors entirely out of an ultra-clean fluoropolymer. One such detector was operated inside a welded, He leak tight, all-fluoropolymer chamber. The measured energy resolution for 570 keV gamma rays is $\sigma/E = 5.1\%$ at a drift field of 1.5 kV/cm, in line with the best values obtained for ionization only detectors run in LXe using conventional, metal vessels. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

For over a decade, plastics have been studied and used as structural materials for particle detectors requiring ultra low levels of radioactive contamination by experiments such as Chooz [1], Palo Verde [2], SNO [3], Borexino/CTF

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[4], KamLAND [5], and MUNU [6]. In these detectors, acrylic, nylon, and EVOH⁴ were used for the containers of the innermost, active liquid volumes. Because of their light weight, low atomic mass, and production processes that involve efficient chemical separation stages, selected plastics have generally shown very low levels of long-lived radioactivity and, particularly, of the naturally occurring heavy metals ²³²Th, and ²³⁸U and, in certain cases, of ⁴⁰K. Contrarily to what occurs in metals, long-lived radioactive

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⁴Ethyl vinyl alcohol derivative film.

isotopes are not produced by nuclear interactions of cosmic rays with most plastics.

EXO ("Enriched Xenon Observatory") is a program [9] aimed at building a ton-class double beta decay detector with 136 Xe. The plan is to use enriched xenon (80% 136 Xe) as source and detection medium. While the EXO collaboration is planning to build a ton-scale detector with the ability to retrieve and identify the ¹³⁶Ba atom produced in the $\beta\beta$ decay of ¹³⁶Xe, an intermediate scale (200 kg of enriched xenon, 80%¹³⁶Xe) detector without the Ba tagging feature, called EXO-200, is currently under advanced construction [10]. The Xe in EXO-200 (and, possibly, in the full size EXO) is kept in liquid phase (LXe) at a temperature around 170 K and a pressure of 1 atm. The two electrons produced in the $\beta\beta$ decay are detected in an electric field of 1-4 kV/cm by the simultaneous readout of ionization and scintillation. This technique has been shown to provide superior energy resolution [11], as required to suppress backgrounds without sharp energy features, such as the $2\nu\beta\beta$ decay of ^{136}Xe and γ -ray Compton tails. In EXO-200 the vacuum ultraviolet (VUV) scintillation light (175 nm) is detected by "bare" (i.e. without their standard encapsulation) large area avalanche photodiodes (LAAPDs),⁵ while the ionization signal is collected by crossed wire grids, hence measuring the total energy of the decay and its three-dimensional location. The third dimension is provided by the drift time using the scintillation signal as the start time. The active LXe has the shape of a cylinder about 40 cm long and 40 cm in diameter. The vessel with the LXe is submerged in HFE- 7000^{6} contained in a low activity, copper cryostat. The HFE-7000 is an ultra-clean fluid that is in liquid phase in a broad range of temperatures, encompassing 300 and 170 K. This fluid is used as the innermost γ and neutron shield and as the thermal bath to maintain a uniform temperature around the LXe vessel. The presence of a large thermal mass of HFE-7000 fluid makes it possible to use xenon containers with poor thermal conductivity such as plastics or thin metallic shells.

The end-point energy for the $\beta\beta$ decay of ¹³⁶Xe (2457.8 keV [12]) is substantially higher than that of most, but not all, radioactive decays in the ²³⁸U and ²³²Th decay chains. In addition, ⁴⁰K and other less common backgrounds are also relevant for a clean reconstruction of the broad energy distribution of the $2\nu\beta\beta$ decays. The high monetary value of the enriched Xe makes it impractical to use it for shielding the detection volume from background events originating from the xenon vessel material. The intrinsic background requirements for all construction components and, in particular, the relatively heavy LXe vessel are therefore very challenging to achieve. Additional constraints are given by the cryogenic temperatures and the

LXe purity requirement with respect to electronegative contaminations, which would reduce the electron lifetime in the detector. Polycarbonate has been used for cryogenic, hermetic vessels, most notably in small bubble chambers [7], because of its mechanical stability, strength, and compatibility with low temperatures. Unfortunately all polycarbonate samples (both in the form of raw pellets and molded plates) measured by our group [8] have shown undesirable levels of radioactive contaminations (especially 40 K), disqualifying them for use in EXO-200.

In this paper we discuss the use of a particular fluoropolymer for the construction of a large cryogenic vessel containing the LXe. We also present data from an ionization chamber built entirely out of such fluoropolymer. Structural performance and details of the construction technology used for the chamber will be the subject of a future publication [13]. Although copper was ultimately chosen for the first generation EXO-200 chamber for scheduling reasons, an evolution of the fluoropolymer chamber described here may be used at a future stage of EXO and by other groups.

2. Fluoropolymer as a vessel material

Fluoropolymers such as polytetrafluoroethylene (PTFE) have been used in the past in LXe detectors as VUV light reflectors and volume displacers [14]. It is therefore known that they are compatible with the clean environment required to drift electrons over large distances of LXe. In addition, fluoropolymer parts are generally known to retain their structural integrity at cryogenic temperatures. DuPont Teflon⁷ TE-6472 [15] is a variety of modified PTFE developed for use in the semiconductor industry and hence produced with high purity standards. Blanks are sintered by first pressing fine pellets in a mold and then baking the material at a specific oven cycle. Levels of radioactive contaminants in the raw pellets of a large batch of TE-6472 set aside for EXO-200 have been measured with neutron activation analysis (NAA) and were found to be $(1.65 \pm 0.17) \times 10^{-9} \text{ g/g}$ for K (1σ) , $<0.26 \times 10^{-12} \text{ g/g}$ for Th and $<0.35 \times 10^{-12} \text{ g/g}$ for U, at 95% CL. NAA results for several other elements confirm the extremely low level of impurities in the material. It was found that other batches of the same product consistently have similar levels of purity. The process of sintering performed on these other batches, once appropriate quality control procedures are implemented, does not appear to degrade the purity and K, Th, and U contaminations of, respectively, $<2 \times 10^{-9}$, $<8 \times 10^{-12}$, and $<3 \times 10^{-12}$ g/g have been measured for finished products. Further tests of sintered parts made with the EXO-200 batch of TE-6472 are currently in progress with higher sensitivity. Final parts are obtained by conventional machining followed by an etch

⁵SD155-9718—16 mm Deep UV LAAPD from Advanced Photonix Inc., Camarillo CA, USA.

 $^{^{6}}$ Novec R Engineered Fluid HFE-7000 (C₃F₇OCH₃) is a fluorinated heat transfer fluid by the 3M Company, St. Paul, MN, USA.

 $^{^{7}}$ Teflon **(R**) is a registered trademark of E.I. du Pont de Nemours & Company. DuPont Teflon TE-6472 is a pelletized form of DuPont Teflon NXT-75, and is now commercialized as DuPont NXT-85.

and rinse that remove possible surface contaminations left by the cutting tools. Most high grades of fluoropolymers from other suppliers were found not to reach the purity levels observed in TE-6472, which are among the very best ever measured in solid materials. Detailed comparison of radioactive contaminants in several plastics and many

other materials will be reported in the near future [8]. An important property of the TE-6472 fluoropolymer is the addition of a small amount of a perfluorinated monomer, or modifier, to standard PTFE to turn it into a weldable material [16]. In addition, the modifier reduces micro-void content and porosity that results in a more homogeneous finished product than conventional PTFE. This pelletized grade of modified PTFE is considered free flowing, and distributes uniformly in a mold with minimal handling. This is in contrast to fine-cut PTFE resins that must be conditioned to loosen their flour or clay-like consistency prior to molding operations. Reduced handling of the resin in the manufacturing environment helps maintain the high purity of the raw material. The specific gravity of finished TE-6472 is 2.2 g/cm^3 (at 20 °C). The welding of finished parts together is carried out by heating the material (up to approximately 380 °C) while applying evenly distributed pressure (somewhere in the range 20-35 kPa is adequate in most cases). We underline that many PTFE welding techniques are determined by trial and error. Each geometry is unique and requires observation to determine the optimal pressure to apply. Excessive pressure, in some circumstances, can create unwanted distortion at the mating surfaces and produce an inferior joint. Weldability is essential for our purpose since it makes it possible to seal the vessel hermetically, without the use of flanges, gaskets, or fasteners. Substantial amounts of material can thus be removed from locations close to the fiducial volume of the detector and the difficulty of sealing the detector using materials with vastly different coefficients of thermal expansion (in this case modified $PTFE^{8}$ and metals) is eliminated. The possibility of fusing parts together also allows for the construction of large components from smaller elements. This is important considering the increasing difficulty of compression molding large parts in one piece, a process that requires a high tonnage press with substantial platen-to-platen clearance and ram travel to accommodate the typical 3:1 powder compression ratio.

Most physical properties of modified PTFE TE-6472 are essentially the same as those of standard PTFE. Modified PTFEs typically have better deformation properties under load [17] and their packing requisites in the molds are more compliant when the raw material comes in pelletized form. Other mechanical properties, such as tensile strength and plastic deformation (some of which we measured for TE-6472 [13]) do not change from average PTFE values. Dielectric constant and strength are also as good or better than those of conventional of PTFE.⁹ Finally, the reflectivity and diffusivity for VUV Xe scintillation light of TE-6472 are currently being measured by our group and will be published in the near future.

3. An all-fluoropolymer detector vessel

In the course of this program several types of allfluoropolymer LXe time projection chamber (TPC) prototype vessels were built. The sketch of one of them is shown in Fig. 1. The vessel is comprised of two halves which are welded together to form a cylindrical cell of 7.9 cm inner diameter and 8.8 cm inner length. The wall thickness is 0.8 cm. Two long pipes made out of a similar type of modified PTFE¹⁰ as that of the vessel are welded to special socket features at both ends. These commercially available pipes are 2.5 and 1.9 cm in outer diameter, respectively, with a wall thickness of 3 mm. They have similar welding properties but were not screened for radioactivity. The ability to make long pipes from TE-6472 was developed for later prototypes. Two pipes (inlet and outlet) are included in order to allow for inline recirculation and purification of the xenon because of the expected outgassing of electronegative impurities from the fluoropolymer walls of the vessels. Moreover, having access to the detector via two pipes allows one to route the cathode high voltage feed separately from the wiring used for lower voltage bias and signal connections at the anode end of the detector (see Section 6). As discussed below, it was later found that Xe continuous purification is not necessary.

The vessel's construction involves several different welds that are performed in a specialized shop using ovens and localized heater bands and plates. Each half-body is machined from stock shapes that are fabricated by fusing tube and solid round preforms together to obtain the required size, or sealed rough form. This approach minimizes material waste and is scalable to larger parts. Socket welds are then performed to connect pipes that then transition to the metal piping of the xenon system, as described below. All-fluoropolymer parts are carefully cleaned with ethyl alcohol and acetone in a class 1000 clean room. The detector instrumentation (ionization cell with LAAPDs and temperature sensors, described in Section 6 and shown in Figs. 1 and 2) is then inserted into the vessel that is subsequently closed with a circular field weld using a hot clamp. In the vessel shown in Fig. 1 the field weld is made using a disk-like feature designed to have enough compliance to accommodate rather large, temporary thermal distortions during the weld. The final assembly and welding were not performed in a clean room environment. Vessels built with this technique can be

 $^{^8} The thermal expansion coefficient of PTFE is <math display="inline">2 \times 10^{-4} \, K^{-1},$ much larger than that of metals.

 $^{^{9}}$ The dielectric strength of DuPont Teflon NXT, a very similar modified PTFE to TE-6472, is 208 kV/mm, while that of conventional PTFE is 140 kV/mm [18].

¹⁰Dyneon® modified PTFE TFR-1105 by the 3M Company, St. Paul, MN, USA.



Fig. 1. Cross-section of the all-fluoropolymer LXe vessel with the welding fixture schematically shown on the left. The upper and lower halves are machined to their final shapes, including the weld flanges with their thermal expansion-compliant regions. A different type of "socket" weld is used to couple straight pipe sections to the ports on the top and bottom of the vessel. TE-6472 supports, independent from the vessel construction, are used to support and space the electrodes in the stack and the LAAPD package. The drift distance (between cathode and grid) is 2.5 cm. All stainless steel electrode planes and rings are 3 mm thick. A ²⁰⁷Bi electron capture source is mounted at the center of the cathode plane.

opened by cutting the material near the field weld with an appropriate guided blade. While the vessel used in this study (Fig. 1) does not have extra material for rewelds, subsequent prototypes (such as the one shown in Fig. 3) were built in such a way as to be re-welded several times [13].

The temperature inside the fluoropolymer vessel, monitored with resistance temperature detectors (RTDs) during the welding cycle, was kept below the maximum recommended storage temperature of the LAAPDs of 150 °C using an abundant (0.61/s) nitrogen flow through the chamber. Problems were encountered with a drastic reduction of the VUV quantum efficiency of the LAAPDs that had been sealed inside the welded fluoropolymer chambers (see Section 4). A sequence of tests, described in Section 4, lead to the specific geometry shown in Fig. 3, which completely eliminates the problem by efficiently purging the fluoropolymer off-gas products before they have a chance of reaching the LAAPDs.

Because of the relatively large permeability of fluoropolymers to He at room temperature, leak checking of the



Fig. 2. Photograph of the electrode stack and LAAPD package. The five electrodes are, from the bottom (see Fig. 1): cathode, grid, anode grid, LAAPD front plane, and LAAPD back plane. Supports independent of the chamber vessel are built using the same TE-6472 fluoropolymer. The ²⁰⁷Bi source is visible at the center of the cathode plate. RTDs can also be seen above the top plate and below the cathode.

finished vessels with He leak detectors requires some care. Experience has shown, however, that the onset of the signal from diffusion, for fluoropolymers of any reasonable thickness, is much slower than that of a real leak, so that a clear discrimination between the two phenomena is easily achieved. It was generally found that the fluoropolymer vessels with their welds and fluoropolymer plumbing are very reliable and He leak tight even after several cycles from room temperature to 170 K. Prototype chambers could be pumped down to $\sim 10^{-5}$ Torr at room temperature in less than 1 h, enough to perform He leak checking. Typical He leak rates, at both room temperature and 170 K are $<5 \times 10^{-9}$ Torr l/s, limited by base pressure and He diffusion through the fluoropolymer walls [13]. No positive He leak was observed in any of the five test chambers that were tested. The ultimate pump-down pressure is determined by permeation through the fluoropolymer walls and is a strong function of temperature, wall thickness, and gas species. The case of the HFE-7000 cryogenic fluid, of direct interest for EXO-200, is specifically discussed in Section 5.

Cryogenic fluoropolymer-to-metal transitions are required in order to interface the all-fluoropolymer vessel to more conventional metal plumbing. Reliable transitions



Fig. 3. Cross-section of a fluoropolymer chamber designed to isolate and purge the welding fumes from the LAAPDs. Arrows indicate the path of a 61/min Ar purge, active during the weld and the cool-down period. Note that in this particular version of the vessel the field weld is achieved by radial (as opposed to longitudinal) compression. For simplicity, threaded fittings not suitable for a cooldown were used for this test of welding compatibility with LAAPDs.

for ~ 2.5 cm diameter pipes have been obtained by pressing a modified stainless steel Curvac flange¹¹ onto a smoothly machined flat surface of the TE-6472 material, as schematically shown in Fig. 4. Using a linear pressure on the circular edge of the flange of 82 kg/cm, the circular cross-section of the Curvac feature penetrates the fluoropolymer up to about half of its radius. A stack of elastic washers insures a constant force against the seal as materials contract or expand and, over long periods of time, creep (in the case of fluoropolymers). Note that, as temperature changes, the Curvac feature "glides" radially on the fluoropolymer surface, without apparent loss of the seal. Transitions built with this technique have been shown to work reliably between 380 and 170 K even after several temperature cycles. Although the transitions are rather bulky, where radioactive backgrounds are a concern they can be located far away from the active region of the detector behind shielding material by providing long fluoropolymer tubes.

A finished chamber is shown in Fig. 5. The fluoropolymer parts of the fluoropolymer-to-metal transitions are



Fig. 4. Schematic drawing of the cryogenic fluoropolymer-to-metal seal. The modified stainless steel Curvac flange (see text) is pressed against a fluoropolymer mating flat with constant force.

visible at the ends of the pipes. Electrical wires, insulated with PFA¹² jackets are also visible (in plastic bags to maintain cleanliness). The tube with the "U" bend is located at the bottom of the cryostat containing the cold HFE-7000 and the two fluoropolymer-to-metal transitions are mounted near the top flange of the cryostat (Fig. 6). All wiring goes through the transitions and onto conventional metal-ceramic feedthroughs branching off the xenon feed lines. We note that because of the poor heat conduction of fluoropolymers, a large chamber built with this technique would require an external Xe condenser.

During welding, the heated region experiences some deformation, which has to be accounted for and controlled by appropriate fixturing. In general, deformation of fluoropolymers does occur during both localized welding and oven fusion. Material shrinkage and elongation varies according to the pressure created by clamping fixtures used during welding. The molding axis and the direction of travel of the compression molding ram, also plays a role in material movement during oven sintering. A variety of factors affect the final geometry of a welded part once cold and will be addressed in a future paper [13]. In the case of the chamber shown in Fig. 1, the thickness of the fused flanges shrinks approximately 8-10%. A similar shrinkage occurs when attaching plumbing using a socket welding technique. The typical maximum working temperature of PTFE (and TE-6472) is 290 °C. The melting point is at about 342°C, and sintering is typically achieved in a temperature range of 365-380 °C. Some material degradation begins to occur during sintering, and temperatures above this range should be avoided [19].

The scalability of fluoropolymer vessels to accommodate larger size detectors, on the scale of EXO-200, has been extensively considered during this R&D effort. While most details are beyond the scope of this paper and will be

¹¹Curvac is a trade mark of ULTEK Corp (Palo Alto, CA) and it refers to a vacuum flange similar in size to the 2-3/4-in. Conflat, but with a rounded-profile sealing edge instead of a knife edge.

¹²Perfluoroalcoxy (PFA) polymers are thermoplastic perfluorinated polymers often used for extruded tubes and sheets.



Fig. 5. Photograph of a finished chamber of the type illustrated in Fig. 1. The two pipes are used for xenon recirculation and as conduits guiding the detector wiring to the outside. Electrical feedthroughs in this prototype are conventional (metal-ceramics), mounted past from the fluoropolymer-to-metal transition. The high bias voltage ($\sim 5 \text{ kV}$) required for the cathode is fed through the pipe opposite to the one feeding the anode, grids and APD potentials and signals.



Fig. 6. The fluoropolymer LXe chamber of Fig. 5, connected to the xenon feed and recirculation system, being inserted into the cryostat. The two fluoropolymer-to-stainless steel transitions of the type drawn in Fig. 4 along the inlet and outlet Xe lines are visible.

discussed elsewhere [13], we note that the primary challenge to the scalability to large chambers is the availability of compression molding equipment capable of molding large stock material components. Techniques are being developed to fuse smaller building block components into larger vessels.

4. Off-gas from fluoropolymers during welding

Following the significant VUV quantum efficiency reduction experienced by the LAAPDs that were welded in the fluoropolymer chamber shown in Fig. 1, a series of tests were conducted to study the effect on such devices of fluoropolymer off-gas, released during the welding cycle. It is known that a variety of chemically reactive fumes, in the form of both aerosols with active radicals and chemical species, are emanated from fluoropolymers at their welding temperatures [20]. Once produced, these fumes can directly react with surfaces or coalesce into larger particles that can then deposit onto detector components. It was shown by health-related studies that the surface of such particles tends to be extremely reactive [21]. For this set of tests, the heat-generating field weld was moved away from the active volume of the detector. Silicon-bronze wire harps and Cu coupons, as well as LAAPDs, were placed inside the test chambers during the welds.

In a first set of tests the fluoropolymer chambers were welded while exposed to air atmosphere. The temperature of the test samples during the welds never exceeded 80 °C. Scanning electron microscope (SEM) images of the surfaces after the weld revealed signs of chemical corrosion and the presence of micron-size debris on the phosphor bronze wires (Fig. 7, top). Energy-dispersive X-ray (EDX) analysis of the visibly corroded areas and of the deposited particles show clear fluorine, carbon, and oxygen content, tracing its origin to the fluoropolymer (Fig. 7, bottom). Because of the possibility of water vapor, oxygen, and nitrogen-related reactions with fluoropolymers [22], argon



Fig. 7. SEM images of a $100 \,\mu\text{m}$ phosphor-bronze wire placed in a fluoropolymer vessel during welding in ambient air atmosphere. Micron-size, surface particulate is clearly visible (top left and, enlarged, top right). Such particles are mainly composed of carbon, fluorine, and oxygen, as shown by EDX elemental analysis (bottom). Their origin is attributable to fluoropolymer fumes reacting with air at high temperature and then re-condensing on the metal surface.

was used as purge gas for further tests. Phosphor bronze wires and Cu coupons welded with a generous Ar purge (0.61/s) showed no surface traces of fluoropolymer off-gas. The test was performed with and without active water cooling applied around the body of the fluoropolymer chamber, with no significant difference. In all cases, the temperature of the test samples never exceed 80 °C. It was also noted that tests performed in this configuration yielded chlorine-rich surface deposits when the metal parts were not thoroughly cleaned prior to the weld. While the exact mechanism for the Cl production is not known, this phenomenon confirms the high reactivity of hot fluoropolymer off-gas and underlines the need to carefully select materials and to clean parts prior to welding. We found standard cleaning procedures for UHV metal components (i.e. ethanol and acetone ultrasonic baths) to be adequate.

Using the wire and Cu samples as tracers for the problems encountered with the LAAPD quantum efficiency degradation, a specific variation of the field weld layout shown in Fig. 3 was developed. This new geometry results in low temperature for the detector components during welding, inert atmosphere, and effective purge of fluoropolymer off-gas products before they come in contact with sensitive components. In particular, the flow pattern for the purge gas is such that off-gas fumes from the weld area are channeled through a pump-out port before they have a chance to reach the LAAPDs. Two LAAPDs were welded in the chamber illustrated in Fig. 3, for which an Ar purge was used. The unaltered VUV response of one of the two devices is shown in Fig. 8; neither device suffered any degradation of their VUV response. The figure also shows the VUV response of a control LAAPD and of devices welded in fluoropolymer vessels with flowing nitrogen and stagnant Ar. The LAAPDs welded in stagnant Ar at 80°C and flowing nitrogen at 150 °C are almost insensitive to VUV scintillation light. The modest Ar purge flow rate (0.11/s) required in the welding setup of Fig. 3 is directly applicable to an EXO-200 scale fluoropolymer detector.

5. Permeation of HFE-7000 in fluoropolymers

Permeation of HFE-7000 through the fluoropolymer walls of the chambers was thoroughly investigated because of the implications of electronegative contamination of the LXe. Long term permeation measurements were



Fig. 8. Response to VUV Xe scintillation light for various LAAPDs. The light source used is a gaseous Xe luminescence cell triggered by an electrical discharge at 1 atm. The initial peak, used for normalization, is due to the prompt, mostly visible light produced by the discharge. The subsequent, broader peak is due to VUV scintillation produced by electrons freed by the discharge as they drift in an electric field. Trace 1 shows the response of a reference LAAPD that was not installed in welded fluoropolymer chambers. Trace 2 is relative to one of three LAAPDs, visible in Fig. 2, mounted in the chamber in Figs. 1, 5, and 6 that was welded in nitrogen atmosphere. Trace 3 shows the response of a LAAPD installed in a chamber like the one illustrated in Fig. 3 and welded in stagnant Ar atmosphere. Finally, trace 4 shows the response of a LAAPD installed in a chamber of the type in Fig. 3 but welded under Ar purge. Clearly the VUV quantum efficiency of devices 2 and 3 is compromised, while the device 4 survived well the welding operation.

undertaken in two fluoropolymers (DuPont PFA-440HP and 3M modified PTFE TFM-1700), considered early on as most promising candidates. Only many months later was TE-6472 fluoropolymer selected as the most suitable choice material for a LXe vessel and then shorter term test were made to verify that HFE-7000 permeation into TE-6472 was similar to with that of the other materials.

Dog-bone-shaped samples, 1.6 mm thick, 38 mm long, and 15 mm wide were immersed in HFE-7000 at room temperature and their weight recorded as a function of time, until saturation was reached. Data for TFM-1700 and PFA-440HP are shown in Fig. 9: full saturation is reached after 1.5 and 5 months, respectively. Data were analyzed assuming a purely diffusive intake into a slab with infinite, parallel walls. This assumes that HFE-7000 intake through the edges of the sample, which constitute ~15% of the exposed surface, is negligible. The effect of such approximation is to overestimate the permeation rate, yielding a slightly conservative result. The solution for the fractional weight gain versus time $\lambda(t)$ is (see e.g. Ref. [23] for a derivation):

$$\lambda(t) = S\left[1 - \frac{4}{\pi^2} \sum_{n=1}^{\infty} \frac{1 - (-1)^n}{n^2} e^{-(n\pi/L)^2 Dt}\right]$$
(1)

where S is the solubility parameter (i.e. the saturation amount of HFE-7000 expressed as fraction of the initial weight of the sample), L the thickness of the sample, and D



Fig. 9. Time evolution of HFE-7000 permeation into TFM-1700 (a modified PTFE similar to TE-6472) and PFA-440HP. The data were taken with a thin sample and are fit assuming diffusion into an infinite, parallel plate slab (see text).

the diffusion coefficient. A fit to the data yields, for TFM-1700, $S = (4.4 \pm 0.2)\%$ and $D = (1.9 \pm 0.7) \times 10^{-9} \text{ cm}^2/\text{s}$, while, for PFA-440HP, $S = (4.4 \pm 0.5)\%$ and $D = (5.9 \pm 2.1) \times 10^{-10} \text{ cm}^2/\text{s}$.

A second test of the permeation properties of HFE-7000 through fluoropolymers was performed by exposing one side of a 0.7 mm-thick PFA-440HP membrane to HFE-7000 at room temperature while pumping out the other side. The evacuated volume was sampled with a residual gas analyzer (RGA) measuring characteristic HFE-7000 mass peaks (e.g. 69, 81, 90, 119, 131 amu). A value $D = 3 \times 10^{-10} \text{ cm}^2/\text{s}$, in good agreement with the measurement above, was obtained by measuring the time needed for the 81 amu concentration to reach 95% of the saturation level (*S* was not determined during this measurement).

Samples of TFM-1700 and PFA-440HP were also tested by immersion at room temperature, with limited accuracy, for permeation of two more heat transfer fluids, FC-87 and HFE-7100,¹³ that had also been considered for use in EXO-200. It was found that $S \sim 5\%$ for HFE-7100 and $S \sim 9\%$ for FC-87 , for both fluoropolymers. D ranges between $\sim 3 \times 10^{-10} \text{ cm}^2/\text{s}$ for HFE-7100 in PFA-440HP and $\sim 2 \times 10^{-9} \text{ cm}^2/\text{s}$ for FC-87 in TFM-1700, consistent with PFA-440HP being less permeable than TFM-1700. Permeation tests were also performed on TFM-1700 samples cooled down to -8 °C. While saturation had not yet been reached at the time of writing, data suggest that S is larger by possibly $\sim 50\%$, while the diffusion coefficient is more than 10 times smaller than that at room temperature. TE-6472 is a modified PTFE much like TFM-1700, and the permeation properties of the two are expected to be similar. Short term tests were performed in order to compare TE-6472 and TFM-1700, suggesting

¹³Fluorinert® FC-87 (C_5F_{12}) and Novec® Engineered Fluid HFE-7100 ($C_4F_9OCH_3$) are products of the 3M Company, St. Paul, MN, USA.

Table 1 Measured values for solubility and diffusion constants of heat transfer fluids in fluoropolymers considered for the EXO-200 xenon chamber

Sample	Method	<i>S</i> (%)	$D (10^{-10} \mathrm{cm}^2/\mathrm{s})$
TFM-1700/HFE-7000	Immersion	4.4 ± 0.2	19 ± 7
TFM-1700/HFE-7000	Immersion $(-8 \pm 2 \circ C)$	~ 6	≤1.9
PFA-440HP/HFE-7000	Immersion	4.4 ± 0.5	5.9 ± 2.1
PFA-440HP/HFE-7000	RGA	-	~3
TFM-1700/FC-87	Immersion	\sim 7.8	~ 20
PFA-440HP/FC-87	Immersion	~9.5	~8.7
TFM-1700/HFE-7100	Immersion	~5.5	~ 8.7
PFA-440HP/HFE-7100	Immersion	≥4.0	≤3.5
TE-6472/HFE-7000	Immersion	\sim TFM-1700/HFE-7000	

Approximate values have large errors due to low statistics or large systematic uncertainties (see text). Most tests were performed by immersing fluoropolymer samples in heat transfer fluids and measuring their weight versus time (see Fig. 9). One test ("RGA") was performed by observing the amplitude of characteristic mass peaks versus time on the evacuated side of a thin fluoropolymer sample in contact with heat transfer fluid on the other side. Unless otherwise specified, tests were performed at room temperature.

a lower value for TE-6472 of possibly $\sim 10\%$, although error bars do not allow to definitively confirm this. Measured solubility values and diffusion coefficient for combinations of fluoropolymers and heat transfer fluids are summarized in Table 1.

As a final, crucial test, a sample of TE-6472 soaked in HFE-7000 was inserted in a LXe cell, operated as a xenon purity monitor. The cell, similar to the one described in Ref. [24], has a long drift region, which allows it to measure electron drift times up to 4 ms. The cell containing the sample was evacuated and cooled down prior to xenon liquefaction. The intensity of the HFE-7000 mass peaks in vacuum was measured versus temperature, providing information on the HFE-7000 emanation rate. Below 247 K, no HFE-7000 signal could be detected above the RGA background ($\sim 10^{-12}$ Torr partial pressure for mass 81 amu). The data above 247 K show a 10-fold reduction in the permeation rate for every 10.5 K decrease in temperature as shown in Fig. 10. An extrapolation to 170 K indicates a negligible release into the LXe. The measured electron lifetime after some purification stabilized at 2.5 ms, consistent with lifetimes obtained with TE-6472 samples not soaked in HFE-7000, indicating that the residual contamination is not increased by HFE-7000 out-gassing. 2.5 ms lifetimes were stably observed for the measurement time of 1 week.

TE-6472 was selected over other candidates for its extremely high radio-purity, lower viscosity at 170 K, good mechanical properties, and weldability. Although it shows a higher permeation rate to HFE-7000 than PFA-440HP, the results of the test in LXe qualify it as a usable material for the EXO-200. Finally we note that the intake of fluorinated fluids causes fluoropolymers to swell and deteriorates their mechanical properties. Our study shows that TFM-1700 and PFA-440HP linearly expand $\sim 3\%$ when saturated with FC-87 or HFE-7100. A twofold reduction of their bulk modulus and yield strength is also observed; such degradation, largest for TFM-1700 in FC-87 and smallest for PFA-440HP in HFE-7100,



Fig. 10. Temperature dependance of HFE-7000 permeation through TE-6472. The permeation falls exponentially as the temperature decreases, with a 10-fold reduction every 10.5 K. The data point at room temperature was not included in the fit.

has to be taken into account when designing structural components.

6. Operation of an all-fluoropolymer liquid xenon ionization chamber

An ionization chamber (Fig. 2) was run inside a fluoropolymer vessel of the kind displayed in Figs. 1 and 5. Because this test occurred relatively early in the R&D program, the purge (nitrogen in this case) provided during the field weld to seal the detector was not optimized to keep the teflon off-gas products away from the LAAPDs, which were degraded as explained in Section 4. As illustrated in Figs. 1 and 2, the ionization chamber consists of an LAAPD package and three horizontal stainless steel structures stacked vertically, submersed in 0.51 of LXe. Electrodes and LAAPD planes are held together by three TE-6472 stand-offs. The stack is loosely placed inside the fluoropolymer chamber, with no rigid connection to it. Ionization electrons created by ionizing radiation in the xenon volume between the lowest plane (cathode) and the grid directly above it are collected at the anode behind the grid. The cathode consists of a solid stainless steel plate, whereas the grid and anode are made of electro-formed nickel meshes with 90% optical transparency, mounted on stainless steel rings. Good electron transparency is obtained by maintaining the anode-to-grid field at twice the value of the drift field. Three LAAPDs, located above the anode plane, detect scintillation photons, as already reported by other groups [25]. However, in the measurements shown here, the quality of the signals from the LAAPDs was rather poor because of the damage caused by the early welding process. Therefore LAAPD signals were only used for triggering and timing purposes and not for energy reconstruction. Later welding tests that preserved the full functionality of LAAPDs were performed, for simplicity, in setups with no grid structure, as explained in Section 4.

After seal-welding the vessel and connecting it to the Xe feed and recovery plumbing (Fig. 6), the entire system is baked at 380 K under vacuum for several days. During this operation the interior of the cryostat is purged with Ar so that no air or water vapor can diffuse into the walls of the fluoropolymer vessel and, eventually, contaminate the xenon. After the system is returned to room temperature, the Ar in the cryostat is replaced with HFE-7000 and cooling is started. Cooling is carried out by flowing liquid nitrogen in a copper line in contact with the liquid HFE-7000 inside the cryostat. During the cooldown the fluoropolymer chamber is kept under vacuum. When the whole system (HFE-7000 + chamber) is stable at 170 K xenon is allowed in the fluoropolymer chamber where it condenses. Xenon is purified in gas phase by passing it through an Oxisorb cartridge¹⁴ eight times. While hot zirconium getters are typically used for low background experiments, Oxisorb, known to introduce radon contamination in the xenon, was adequate for this test. Filling the fluoropolymer with LXe (approximately 0.51) in our setup without an external condenser, takes about 6 h. Condensation of the same amount of Xe in a pre-cooled, similarly sized Cu chamber for prior tests in the same cryostat took only about 2 h. All the data shown here were taken between 165.5 and 171 K and between 1200 and 1470 Pa.

Ionization in the LXe is produced by both the 570 and 1064 keV γ -ray lines following the β decay of ²⁰⁷Bi as well as by internal conversion (IC) electrons. The 0.5 and 1 MeV electrons have a range of approximately 1 and 3 mm, respectively, in LXe [26]. A source is prepared as a submonoatomic layer of radioactive Bi electroplated onto a 25 mm² piece of electroformed nickel mesh, which is then spot-welded to the center of the cathode plate. The data presented here were collected at drift fields of 0.25, 0.5, 0.75, 1, and 1.5 kV/cm. Events are selected with drift time

corresponding to the cathode-to-grid distance to obtain a relatively pure sample of IC electrons which all interact in very close proximity of the source. The electron signal at the anode is detected by a low noise, charge-sensitive Amptek A250 preamplifier, followed by a Canberra model 2020 spectroscopy amplifier with a 4 µs shaping time (gain = 210). The three LAAPDs are read out in parallel as one single channel and are biased applying -1550 V to the front side while reading out the signals from the back side kept at ground. An Ortec 142 IH preamplifier followed by an Ortec 570 amplifier (shaping time = $2 \mu s$, gain = 25) was used for the LAAPD signal. The total geometrical coverage of the LAAPDs for events at the center of the cathode is 2.4%; this value does not include the quantum efficiency for Xe scintillation light nor the effect of reflection and diffusion on the fluoropolymer walls. Both the ionization and scintillation signals from their respective shaping amplifiers are sampled with a transient digitizer and recorded. Coincident pulses from a single event are shown in Fig. 11. Special care is required to reduce pick-up noise. An all-fluoropolymer vessel, with no intrinsic metallic shield around the electrodes, is an unconventional layout for an ionization detector. Proper grounding and shielding must be provided by other means (for instance, by the cryostat enclosure).

In the off-line analysis, charge and scintillation light signals are fitted to the following five-parameter analytical



Fig. 11. Ionization (top) and scintillation (bottom) pulses emerging from the shaping amplifiers of each channel for an event. Both pulses are fitted with the function in Eq. (2) (see text for details).

¹⁴Oxisorb[®] cartridge from Messer-Griesheim Gmbh, 47805 Krefeld, Germany.

function:

$$A\sigma \left[\operatorname{erf}\left(\frac{t_0}{\sqrt{2}\sigma}\right) - \operatorname{erf}\left(\frac{-t+t_0}{\sqrt{2}\sigma}\right) \right] \mathrm{e}^{(-t+t_0)/\tau} + B.$$
⁽²⁾

Here A is the amplitude, t_0 the time from the beginning of the sampling window, σ the rise-time, τ the integrator falltime, and B a vertical offset. The ionization readout is calibrated in units of electron charge by injecting a 11.2 mV pulse into the pre-amplifier through a 1pF calibrated capacitor, corresponding to 70,000 electrons. The electronic noise of the pre-amplifier was found to follow a Gaussian distribution with standard deviation of 597 electrons (see Fig. 12). Data acquisition is triggered when a delayed coincidence between scintillation and ionization signals is observed. The drift time of the ionization electrons from their production point in the LXe to the anode is given, event-by-event, by the delay between scintillation and ionization pulses, i.e. $t_{0,ioniz} - t_{0,scint}$. The drift velocity of electrons varies with electric field. The selection of IC events, which occur along the main axis of the ionization cell, alleviates the effects of possible nonuniformities in the electric field across the active volume of the detector, which is not equipped with field-shaping electrodes.

An ionization spectrum obtained at 1.5 kV/cm and the calibration pulse for the ionization readout chain are shown in Fig. 12. The 570 keV peak of the ²⁰⁷Bi spectrum is fit to a Gaussian plus a straight line as shown. The noise-subtracted energy resolution is shown as a function of the drift field in Fig. 13. Such resolution for 570 keV is found to be $\sigma/E = 5.1\%$ at 1.5 kV/cm, in good quantitative agreement with the results obtained by our group and others using conventional construction techniques [27].



Fig. 12. Ionization energy spectrum collected at a drift field of 1.5 kV/cm. The two lower peaks correspond to the two internal conversion electron lines from the ²⁰⁷Bi source, at 570 and 1064 keV (K-shell electron events at 975 keV are also visible as a shoulder to the 1064 keV peak). In order to evaluate the energy resolution at 570 keV, the data is fit to a Gaussian plus a straight line. The 1064 keV peak is not included in the fit. The horizontal axis shows the amplitude of the pulse in Volts (see Fig. 11). The sharper, higher energy peak is obtained by injecting a 11.2 mV pulse in the preamplifier through a 1 pF capacitor, corresponding to 70,000 electrons.



Fig. 13. Ionization energy resolution for 570 keV electrons in LXe at several drift fields. The triangles represent the resolution observed in this experiment. The other symbols represent the resolution for ionization obtained by other experiments [11,27] using chambers of conventional construction.

As mentioned above, because of low LAAPD quantum efficiency, the energy spectrum of the scintillation pulses was poorly resolved and the light was only used for timing purposes. The chamber described here was run for 10 days without re-purification of the LXe. No degradation of the signal amplitude or of the resolution was observed.

7. Conclusions

Fluoropolymer construction of vessels for TPCs using LXe has been demonstrated for the first time. Because of the very low radioactive contaminations in the special fluoropolymer variety discussed here, this exotic technique has great promise for low background experiments detecting charge and/or scintillation light in LXe and, possibly, other liquefied noble elements, most notably LAr.

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