Rigid Polyurethane Foams as External Tank Cryogenic Insulation for Space Launchers

U Cabulis¹, V Yakushin¹, W P P Fischer², M Rundans¹, I Sevastyanova¹, L Deme¹

¹ Latvian State Institute of Wood Chemistry, Riga, Latvia
² ArianeGroup GmbH, Bremen, Germany

E-mail: cabulis@edi.lv

Abstract. In the framework of the present activity, work is carried out on the development of rigid polyurethane (PUR) foam material for external cryogenic insulation of a liquefied hydrogen (LH2) tank for the next generation launcher with a cryogenic upper stage. The main advantage of PUR foams in comparison with other thermal insulation materials is possibility to cover this material on the complicated shape metal surfaces by spraying method, which leads to significant cost savings. The spraying of PUR foams on metal constructions is chemical-technological process. As a result of work performed within the confidential European Space Agency contract, PUR foam material has been developed for the use as external insulation material for fuel tank structures. Raw ingredients from suppliers within EU have been used exclusively. The material has been tested for its performance in normal (room) and relevant (cryogenic conditions) environment and found to be mechanically durable and thermally excellent and therefore appropriate for use in space application. Accelerated ageing test indicate the material to be long-lasting. Safety coefficient, which characterizes the capability of insulation to withstand cryo-shocks, for optimal compositions reaches 4.7.

1. Introduction
The cryogenic insulation is very important for the space launchers with liquefied hydrogen (LH2) and liquefied oxygen (LOX) as the propellants. The basic requirements for the insulation materials are good thermal-insulating performance, especially at low temperatures, light weight and at the same time it must be non-flammable material, since during scent phase significant thermal loads are acting on the surface of the launcher. Although some of these characteristics are quite contradictory. For external thermal insulation (ETI) material additional important characteristics are UV-stability and the material's ability to resist cryo-pumping effects, and minimal outgassing at vacuum conditions. The leading contributors in space activities – USA [1], China [2] and also EU [3] are using cryogenic propellants and therefore, space research centres there are carrying out in-depth studies in the field of cryogenics.

Ever since the development of the vacuum flask, the vacuum is still the primary player in most insulation schemes on ground, where the weight of the system does not play a big role or in stationary conditions, where damage due to loads or vibration is not possible. In space industry there are two main solutions for cryogenic insulation. One common radiation barrier used in cryogenic applications is known as Multilayer Insulation (MLI). The MLI generally contains multiple layers of reflective material also called radiation shields (low emissivity foils, also called screens) separated by spacers having low conductivity (typically 0.25 mm thick) [4]. But, drawback is the poor thermal performance on ground or ascent conditions. The other solution is polymeric foams, which possess many advantageous properties, such as low thermal conductivity, light weight, low water absorption/permeability, and...
dimensional stability and can satisfy thermal requirements for phases where the pressure is above vacuum. In particular, polymeric foams do not change in volume along temperature gradients, in other words, they exhibit significant size stability [5]. Rigid polyurethane (PUR) foams have outstanding properties [6], and some of them are successfully used even today as cryogenic insulation. A combination of both above mentioned materials is also developed for cryogenic insulation [7]. In the future, PUR foams and other plastic foams are regarded as the main material for liquefied gas tank cryogenic insulation in different projects of liquefied natural gas (LNG) carriers [8] and space vehicles [6]. The main advantage of PUR foams in comparison with other thermal insulation materials is possibility to cover this material on the complicated shape metal surfaces by spraying method [9]. PUR foams obtained by spraying method were first developed in the 1960s and included applications for the Saturn V moon rockets and subsequently the Space Shuttle [6].

The properties of PUR foams and their adhesion to substrate materials depend not only on the chemical structure and macromolecule architecture of the polymeric matrix, but also on the technological factors of PUR foam production. PUR foam composition was developed in the frame of the confidential contract with European Space Agency. The tasks of this research were to develop and modify necessary polyol composition for production of spraying cryogenic insulation with optimal technological parameters. The used PU foam composition was calculated and optimised using previously described [10] approach for development of cryogenic insulation. Influence of technological parameters on the physical and mechanical characteristics of the ETI and their modifications was investigated. Also such important properties as flammability and UV-stability of ETI foams were measured.

2. Experimental

2.1 Materials

Cryogenic PUR foam composition (Cryo_PUR) was created combining Lupranol type (BASF) polyether type polyols with functionality 3 and 4 and OH-values 400 and 740 respectively as main ingredients in the recipe; also, reactive and additive flame retardants were introduced in system, and combination between physical (Solkane™ 365/227 (Solvay)) and chemical (water) blowing agents were used. Catalyst package included amine and tin containing catalysts. Desmodur® 44V20L (Bayer) was used as an isocyanate component for all rigid PUR foam samples. It is a solvent-free product based on 4,4′-diphenylmethane diisocyanate (MDI) and contains oligomers of high functionality. The average functionality was 2.8 to 2.9 and the NCO content was 30.5 to 32.5 wt.%. The calculated isocyanate index of composition was 110.

2.2 Sample preparation

Cryo_PUR foam panels were made with the high-pressure spraying machine Glass Craft VR. Cryo_PUR composition was spray-applied in one pass on 4 mm thick aluminium sheets, coated with a wax-based release agent. Aluminium sheets were heated until the desired temperature using an infrared heater. The temperature of aluminium sheets and small aluminum plates for the adhesion test was measured using a special surface thermocouple. Generally, samples for different tests were cut out from the panels’ core. For production of Cryo_PUR foams by spraying method, the following parameters were controlled and maintained: A-component (polyol) and B-component (isocyanate) temperatures and viscosities, A and B components’ volume ratios, pressure at A and B components’ supply lines and also room temperature and relative air moisture.

2.3 Test methods

A Static Materials Testing Machine Z010 TN (Zwick GmbH & Co) for foam testing at 295 K was used. Compression tests were performed in two directions: parallel (Z) and perpendicular (X) to foam rise. To taking into account thickness limitation of sprayed layer, samples of 30×30×30 mm size were used. The testing of the foams’ mechanical properties at 77 K was carried out with a Testing Machine Z100 (Zwick
GmbH & Co). For both tests the basic program testXpert V11.02 was used. A compact cryogenic facility and specific appliances for foam testing at cryogenic temperatures are shown in figure 1. Ring samples, 13-14 mm in width, with the inner diameter 43 mm and the outer diameter 53 mm, were used for tensile characteristics determination. A detailed analysis of this method compared to standard method for determination of tensile strength for foam materials (ISO 1926:2009) has been given in [11]. The adhesion of the Cryo_PUR foam to aluminium (tensile bond strength) was determined after the cryo-shock test (instant immersion in liquefied nitrogen, exposure therein for 60 min and warming at room temperature). The tests were performed according to EN 1607 “Determination of tensile strength perpendicular to faces of Thermal Insulation Products”. The thickness of the foam material between the substrate (aluminium sheet) and the glued pad was 10 mm.

![Figure 1. a) Testing Machine Z100 with a cryogenic testing facility; b) appliance for the rings tensile test; c) appliance for the bond strength determination.](image)

The ETI’s possibility to withstand thermal strains can be characterized by safety coefficient $K_S$, which can be calculated from following equation:

$$K_S = \frac{e_{77}}{\Delta l_{77-295}} = \frac{e_{77}}{\alpha_x \cdot \Delta T \cdot 100}$$

(1)

where:

- $e_{77}$ – PUR foam elongation at 77K perpendicular to foaming direction, %;
- $\Delta l_{77-295}$ – the contraction of PUR foam perpendicular to foaming direction freezing it from 295 K to 77 K, %;
- $\alpha_x$ – coefficient of thermal expansion;
- $\Delta T$ – temperatures difference.

The data for calculation of the average coefficient of thermal expansion (CTE) of the foam were obtained by the means of dilatometric measurements (3 samples) in the range of temperatures from 295K to 110 K using TMA Linseis PT1600 equipment. Only small specimens of $4 \times 4 \times 20$ mm size can be used when using this device.

Thermal conductivity coefficient $\lambda_{10}$ of foams was determined using a Linseis HFM 200 thermal analyser. The size of samples was 200×200×50 mm, top plate temperature 20°C and bottom plate temperature 0°C.

The flammability test of Cryo_PUR foams according to EN ISO 11925-2:2010 “Reaction to fire tests – Ignitability of products subjected to direct impingement of flame – Part 2: Single-flame source test” was performed in an apparatus produced by FTT-Fire Testing Technologies. Foam samples of 250×90×40-50 mm size were cut-out from the core of panels. Flame application time was 30 s.

Artificial ageing has been done using UV accelerated weathering chamber held at 60°C temperature and ambient pressure. A fluorescent lamp UVA-340 (295–420 nm, max 340 nm) with the intensity 0.89 W/m² was used. The degradation experiment was conducted for 5 weeks. Samples were periodically
photographed with a photo camera and SEM. SEM image analysis has been performed using Tescan TS 5136 MM equipment in secondary electron detection mode.

3. Results and discussions
The optimum spraying parameters for developed Cryo_PUR foams and ambient conditions are given in table 1.

| Table 1. Main parameters of Cryo_PUR sample spraying |
|-----------------------------------------------|
| Volume ratio of components A:B             | 1.0 : 1.0 |
| A and B components’ temperature, °C        | 40        |
| A-component viscosity at 25°C, mPa·s       | 450 - 500 |
| B-component viscosity at 25°C, mPa·s       | 200 - 230 |
| Hydraulic oil pressure, bar                | 40        |
| A-component working pressure, bar          | 110 - 130 |
| B-component working pressure, bar          | 130 - 150 |
| Ambient temperature, °C                    | 18 - 20   |
| Air relative moisture, %                   | 40 - 50   |

Three different aluminium sheet temperatures (20; 25 and 30°C) were chosen, since it is known, that at higher substrate temperature the bond strength to surface increases. The basic physical-mechanical characteristics and calculated safety coefficients are given in table 2.

| Table 2. Test results and safety coefficient of spray applied Cryo_PUR foam |
|------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Al sheet temp., °C | ρ, kg/m³         | σys, MPa        | σs, MPa         | Bond strength, MPa | σ77, MPa      | ε77, %          | ΔI77,295, %  | Ks               |
| 20               | 48.7            | 0.238           | 0.184           | 0.46             | 1.21           | 5.66            | 1.23          | 4.61             |
| 25               | 48.4            | 0.220           | 0.187           | 0.74             | -              | -               | -             | -                |
| 30               | 48.8            | 0.219           | 0.176           | 0.62             | 1.20           | 5.92            | 1.29          | 4.66             |

It is confirmed that aluminium substrate sheet temperature does not have a significant influence on the safety coefficient and basic physical-mechanical characteristics. The obtained Ks above 4 is very high, and obtained Cryo_PUR foams from physical-mechanical point of view can be characterised as potential cryogenic insulation material [10].

The obtained dilatometric curves are shown in figure 2. Experimental data can be well enough approximated with a polynomial trend and extrapolated. Contraction level of foams and an average CTE value in the range of temperatures from 295 K to 77 K are calculated to be 1.49% and 68.4·10⁻⁶ K⁻¹ respectively. When comparing the data obtained from TMA PT1600 with the data from cryostat tests, it should be noted that data for calculations are obtained by the means of extrapolation of dilatometric test data. Moreover, the sample limitations for the TMA PT1600 device did not allow to assess the scale effect on the results of measurements as the maximum sample size limit for this device (4×4×20 mm) is obviously too small for cellular materials. Nevertheless, the obtained Ks using TMA analyser is 3.9, which is also high in comparison with conventional foams [10].

Physical-mechanical properties at different temperatures and capability to withstand cryo-shocks are not the only important characteristics for cryogenic insulation; material must be stable in long-term storage and also non-flammable and UV-stable.

The thermal insulation capacity of foam materials isn’t only influenced by chemical structure but also depends on the environmental factors such as temperature, humidity and radiation. In addition, the gas diffusion through the foam struts will result in the thermal insulation performance degradation with time and the aging will be affected by the operating environment [12]. Before long term storage at room temperature, λ_{10} for initial foams was 17.6 mW/m·K, after half a year – λ_{10} increases up to 20.7
mW/m·K (figure 3). The $\lambda_{10}$ for aged conventional PUR thermal insulation materials reaches 26-28 mW/m·K [13], the significantly lower $\lambda_{10}$ of Cryo_PUR was achieved due to the fine cell structure (figure 5b) and chemical composition of foam matrix.

**Figure 2.** Changes of specimen length versus temperature for the Cryo_PUR foam

**Figure 3.** Changes of thermal conductivity coefficient ($\lambda_{10}$) at long term storage

Flammability test according to ISO 11925-2:2010 has been conducted and the results can be seen in table 3 below. Six samples in total were tested from the front and back sides (figure 4). In 3 out of 12 cases flame tip reached the mark of 150 mm, but in all cases the height of the damaged area did not exceed the 150 mm mark. Currently two types of flame retardants, additive and reactive, are being used to prepare polyurethane foams with low flammability [14]. Combination of both was used in Cryo_PUR composition and obtained flammability result turned out to be suitable for space launcher parts, which are subjected to aerodynamic friction.

| $\rho$, kg/m$^3$ | Did sample ignite? | Did flame tip reach 150 mm? | Average height of the damaged area, mm |
|-----------------|---------------------|----------------------------|---------------------------------------|
| 51 ± 3          | Yes – 100%          | Yes – 25%                  | 130 ± 8                               |

**Figure 4.** Partly burned sample of Cryo_PUR foams after flammability test

During UV-irradiation the aromatic structures are oxidized at the central methylene group, leading to highly conjugated quinone products. The accumulation of quinone products due to the chain scission of the PUR macromolecules induces formation of coloured products [15] (Figure 5a), at the same time the weaker polyether chain segments degrade under UV-irradiation. SEM images (Figure 5b) were acquired before and after exposure to UV for determination of thickness of degradation. The cell walls under the influence of UV radiation collapse first but the network of struts remains. It can be assumed that cell walls behave like thin PUR films, but struts are the thickest and most robust parts of the PUR foam. The degraded layer is clearly visible and therefore can be easily measured. Figure 5c presents the thickness of degraded layer during UV exposure. After 2 weeks the level of degradation reached the maximum, and further, deeper degradation is not observed. The thickness of degraded layer is 1.5 – 2 times thinner than for conventional foams, including foams containing renewable raw materials [16].
Figure 5. PUR foam samples before and after 5 weeks of artificial ageing; a) photographs; b) SEM images; c) thickness of degraded layer.

4. Conclusions
Rigid polyurethane foam material obtained by spraying method has been developed for the use as external insulation material for space launcher fuel tank structures. Material can be characterised by high bond strength to aluminium substrate and safety coefficient value reaching 4.7. In the same time the foam exhibits stable properties in long term storage and characterizes as self-extinguishing material. The thickness of degraded layer at accelerated UV-irradiation is less than 0.6 mm. Material is prospective not only for space applications, but also for other cryogenic fields, for example LNG transport.

Acknowledgements
The study was financed by the European Space Agency PECS project CRYOFOAMS, Contract No:4000114532/15/NL/NDe

References
[1] Graham R 2003 External Tank Thermal Protection System (NASA Facts. FS-2003-09-113-MSFC)
[2] Zhang X B, Yao L, Qiu L M, Gan Z H, Yang R P, Ma X J and Liu Z H 2012 Experimental study on cryogenic moisture uptake in polyurethane foam insulation material Cryogenics 52 810–5
[3] Fischer W P P, Stirna U, Yakushin V and Cabulis U 2010 40th Int. Conf. on Environmental Systems (Barcelona) (Reston: American Institute of Aeronautics and Astronautics) 6295
[4] Krishnaprakas C, Narayana K B and Dutta P 2000 Heat transfer correlations for multilayer insulation systems Cryogenics 40 431–5
[5] Bahadori A 2014 Thermal Insulation Handbook for the Oil, Gas, and Petrochemical Industries. 1st ed. (Oxford: Gulf Professional Publishing)
[6] Fesmire J E, Coffman B E, Meneghelli B J and Heckle K W 2012 Spray-on foam insulations for launch vehicle cryogenic tanks Cryogenics 52 251–61
[7] Zheng J, Chen L, Cui C, Guo J, Zhu W, Zhou Y and Wang J 2018 Experimental study on composite insulation system of spray on foam insulation and variable density multilayer insulation Appl. Therm. Eng. 130 161–8
Lee Y, Baek K H, Choe K and Han C 2016 Development of mass production type rigid polyurethane foam for LNG carrier using ozone depletion free blowing agent Cryogenics 80 44–51

Cabulis U, Yakushin V and Fischer W P P 2017 Preparation of rigid polyurethane foams as inner wetted thermal insulation Proc. of PPS-33 (Cancun) (New York: AIP Conference Proceedings) In press

Stirna U, Beverte I, Yakushin V and Cabulis U 2011 Mechanical properties of rigid polyurethane foams at room and cryogenic temperatures J. Cell. Plast. 47 337–55

Zhmud' N P and Yakushin V A 1986 Determination of the properties of rigid polyurethane foams in tension on ring specimens Mekhanika Kompozitnykh Materialov 6 1123–7

Zhang H, Fang W Z, Li Y M and Tao W Q 2017 Experimental study of thermal conductivity of polyurethane foams Appl. Thermal Eng. 115 528–38

Closed and open-cell spray polyurethane (PU) foam 2013 (PU Europe Factsheet No.22)

Bhoyate S, Jonesku M, Radojić D, Kahol P K, Chen J, Mishra S R and Gupta R K 2018 Highly flame-retardant bio-based polyurethanes using novel reactive polyols J. Appl. Polym. Sci. 135 46027

Wilhelm C, Rivaton A and Gardette J L 1998 Infrared analysis of the photochemical behaviour of segmented polyurethanes. 3. Aromatic diisocyanate based polymers Polymer. 39 1223–32

Paberza A, Stiebra L and Cabulis U 2015 Photodegradation of polyurethane foam obtained from renewable resource – pulp production byproducts J. Renew. Mater. 3 19–27