Whitepaper

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FUEL LOCK BLISTER PERFORMANCE AIDS IN *SAFE HYDROGEN TANKS*

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Hydrogen storage is an essential element for the hydrogen driving powertrain of automobiles. Hydrogen as an energy carrier is characterized by its relative high energy density per mass and its relative low energy density per volume. Its relative high energy density per mass is illustrated by the fact that in practice for a passenger car typically 5 kg of hydrogen provides a driving range of 500 km. This is in contrast to gasoline for which typically 30 kg is required. The volume of 5 kg hydrogen at 1 bar and room temperature however is 60 m³. To accommodate for this low energy density per volume, different storage scenarios for hydrogen are feasible. Physical storage via adsorption or absorption in solid media might be considered, but also storage of pure hydrogen under cryogenic conditions or storage under high pressure. For automotive storage applications, it seems the industry embraces the last scenario. Hydrogen is stored in high–pressure hydrogen tanks with typical operating pressures of 700 or 350 bars. Two crucial performance features of these high–pressure tanks are low weight and safety. Low weight is realized by moving away from a metal tank solutions and designing the tank based on polymer–based materials. Safety is realized by a careful selection and development of polymer materials and proper design of the high–pressure tank.

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Currently so–called type IV tanks are being commercialized for this specific application. A type IV tank typically consists of two parts; a full thermoplastic inner liner and a polymer based outer composite shell. The composite might be based on continuous glass– or carbon fibers embedded in an epoxy matrix. This combination of inner liner and composite material provides a light–weight tank. There are several ingredients contributing to the safety performance. The outer composite shell provides sufficient mechanical strength to withstand the high hydrogen operating pressures and sudden impact incidents. The inner liner contributes to safety by providing sufficient hydrogen gas barrier– and blister performance.

This paper is about the hydrogen tank inner liner material with the focus on the safety performance as provided by gas barrier and blister functionality.

Over the last years within Envalior (former DSM Engineering Materials and Lanxess HPM), the so–called Fuel Lock product family has been developed based on world–class (barrier) material expertise and solid product development. One part of this product family is specially developed as inner liner material for hydrogen tank applications and provides state–of–the–art functionality.

BLISTER PERFORMANCE

Fast decompression of the hydrogen gas in the storage tank might lead some polymer materials to blistering of the inner liner.

Blistering is manifested by macroscopic crack formation or whitening of the material and might lead to a reduction of the gas barrier performance. The underlying mechanistic picture is the following: at high hydrogen operating pressures, a certain amount of hydrogen is dissolved in the polymer inner liner material that is in thermodynamic equilibrium with the hydrogen gas. At a lower hydrogen pressure, a lower amount of dissolved hydrogen gas is in equilibrium with the hydrogen gas. As indicated in the permeation section, for PA6 hydrogen solubility scales linearly with pressure. In case lowering of the pressure occurs rather slowly over time, the inner liner material can release the surplus of dissolved hydrogen by macroscopic diffusion to the outside world.

However, in the case of a fast hydrogen pressure quench, the macroscopic diffusion process is not able to follow the pressure quench, leading to an oversaturation of the dissolved hydrogen in the polymer part. Internal hydrogen gas formation might occur via a nucleation mechanism where for instance impurities in the material act as initiators for the gas to be released internally. Also, already existing small cavities or holes could be further inflated by internal gas release. It is believed that nucleation sites or initial cavities have dimensions in the order of micron – or submicron level. The local outgrowth into larger blisters is affected by the local diffusion process of the dissolved hydrogen towards the internal defect but also by the local mechanical resistance of the material for further growth. The mechanical resistance is related to mechanical properties such as the modulus and the yield stress of the material.

Local outgrowth into larger blisters is affected by the local diffusion process of dissolved hydrogen towards the internal defect.

Blister experiments were conducted at Testnet, Munich, Germany. A rather stringent blister protocol was followed that might not be representative for a real tank application but is used by customers to discriminate the blister resistance of polymer materials. The test conditions are the following: injection molded plaques or parts of a blow molded tank with a thickness of 2mm were cut into disks with a lateral diameter of appr. 5 cm. After a drying procedure, the samples were exposed to 1000 bar hydrogen pressure at T=80°C during 14 hrs to ensure full equilibration of the sample in the hydrogen environment. In a period of 30s, the pressure was quenched to ambient pressure. By a visual inspection of the samples (in duplo) after the pressure quench, blister performance was evaluated and ranked into the categories:

- No–blistering indicated by a green color
- Onset of blistering indicated by an orange color
- Severe blistering indicated by a red color

In Figure 1, the blister performance of the pure materials PA6, PA11 and HDPE is given a color code and a photograph of the specimen is shown.

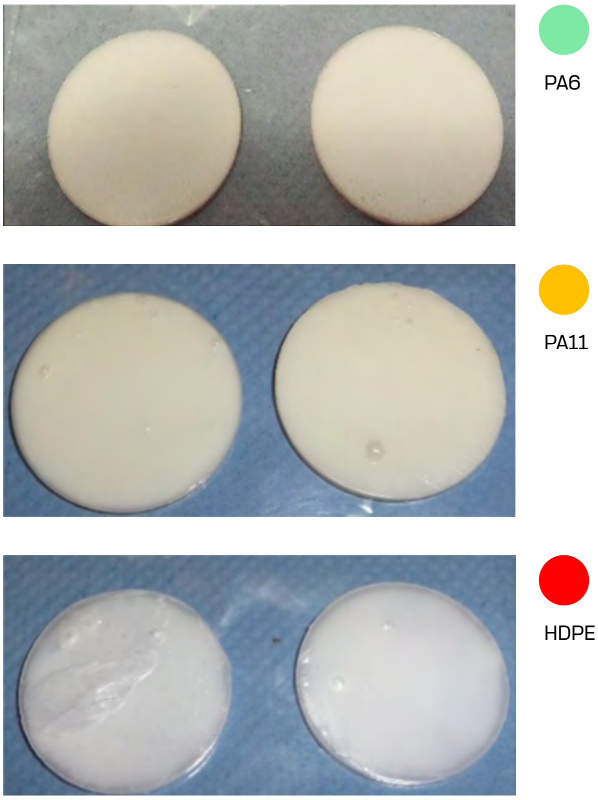

Figure 1
Blister performance of injection molded specimen of PA6, PA11 and HDPE as visualized by photographs of samples and color code (for color code see text).

A visual inspection shows that the PA6 sample is blister free; no visual indications for gas bubble formation whatsoever.

The PA11 sample shows clear visual evidence of blistering as manifested by local indications for gas bubble formation in an area beneath the surface for both samples. For HDPE severe signs for blistering are apparent in both samples since a larger part of the sample surface seems to be affected and damaged. The cause for the inferior hydrogen blistering performance of HDPE and PA11 versus PA6 can be explained by the differences in solubility and diffusion speed of hydrogen in the polymer matrix.

In Table 1 it is shown that the hydrogen solubility in HDPE and PA11 is larger compared to the solubility in PA6. The larger this solubility, the larger the amount of gas that will be in the oversaturated state and more severe blistering is to be expected.

Material	Hydrogen permeation in *10^{-9} mol/m s MPa*	Hydrogen diffusion coeff. in *10–10 m^2/s*	Hydrogen solubility in *mol/m^3 MPa*
HDPE	0.82	1.9	4.3
PA11	0.40	0.65	6.2
Envalior–PA6	0.084	0.29	2.9
FLX40–HP	0.132	0.34	3.9
FLE–LP	0.122	–	–

Table 1
Hydrogen permeation characteristics for Envalior–PA6, FLX40–HP and FLE–LP compared with other materials as measured at room temperature (other materials based on Sandia study (Sandia report SAND2013–8904, R.R.Bart et al, Polymers for hydrogen infrastructure and vehicle fuel systems)).

With respect to the macroscopic diffusion effect, the hydrogen diffusion coefficient in PA6 at T=80°C is expected to be around $2{*}10^{-12}$ m^2/s (see info in permeation section). A Fourier analysis learns that only an outer layer of the polymer sample of less than 0.1 mm thick can release hydrogen to the outside world via macroscopic diffusion within 30s pressure quench (based on Fourier number = $Dt/l^2 = 1$). It is expected that for HDPE the hydrogen diffusion coefficient is roughly 5 times larger compared to that for PA6 leading to the conclusion that this outer layer for HDPE is less than 0.2 mm thick (layer thickness scales with $(Dt)^{1/2}$). This means that for all tested materials, most of the polymer sample is not affected by macroscopic diffusion and will be in an oversaturated state after quenching allowing blister formation to occur.

For a gas bubble to grow further in the material, the microscopic local hydrogen permeation is of importance. In case no microscopic diffusion process would take place, an increase of the bubble size by e.g. a factor of 10 in three dimensions would lead to a gas pressure drop in the bubble by a factor of 10^3. This means that for the given pressure quench from 1000 bar to ambient pressure, the driving force for further growth, being the overpressure, vanishes at the sketched volumetric increase. This would mean that outgrowth to macroscopic blister sizes is not possible unless additional hydrogen is released from the polymer material into the growing blister by a local diffusion process. A polymer material with a higher diffusion speed and higher hydrogen solubility can supply more hydrogen in time towards the growing bubble.

In this view, the outgrowth is facilitated for HDPE and PA11 compared to PA6 in view of the differences in diffusion speed and solubility as sketched in Table 1.

Besides diffusion and solubility aspects, also mechanical properties of the material will affect the formation of blisters.

In the classical picture of Gent (J.Appl.Phys. 40, 2520 [1969]) dealing with bubble inflation in an elastomer, the critical inflation pressure pc leading to infinite bubble growth equals 5/6 E with E the Young's modulus of the material. This picture might explain the very early stages of blister outgrowth for semi-crystalline materials but cannot be applied to later stages in the blister formation since yield phenomena and even rupture processes may be involved. Another limitation in applying Gent's picture to the blister behavior at hand is that for blister formation a local hydrogen supply to the growing blister is required as explained before. Gent's approach deals with bubble inflation due to an external stress state. In view of these limitations however, one could argue that the "mechanical resistance" for PA6 in the first stages of outgrowth is larger compared to HDPE and PA11. This statement is based on the values for the Young's moduli of the different materials, see Table 2.

	PA6	PA11	HDPE	FLE–LP**
E [**MPa**]	520	190	190	325

Table 2
Young's modulus at T=80°C for different materials (based on internal measurements).

For the semi-crystalline materials at hand, an interpretation of blister formation can be made in terms of the yield strength of the material. When the overpressure in an existing cavity or hole exceeds the yield strength of the material, further outgrowth might occur leading to larger scale blisters. In the following table, the yield strength is given:

	PA6	PA11	HDPE
Tensile yield strength [**MPa**] **at T=23oC**	81	36	~20
Tensile yield stress [**MPa**] **at T=77oC**	30	–	–

Table 3
Yield strength for different materials (PA6, PA11, dry as molded: from Nylon Plastic Handbook, Ed.M.I.Kohan, Hanser Publ., HDPE: I.M.Ward et al, J.Polym.Sci.,Part B, 22(2), 191 (1984)).

The yield strength values suggest that PA6 is more resistant toward blister formation compared to HDPE and PA11 but the values also suggest that under the given experimental blister conditions (hydrogen overpressure: 100 MPa, T=80°C) the overpressure exceeds the yield strength, even for PA6. The fact that under the given experimental conditions blistering is not observed for PA6 hints towards the fact that macroscopic outgrowth of a blister might be limited by hydrogen supply via diffusion to the growing blister.

The blister performance was also experimentally studied for two impact modified PA6 grades: FLE-LP (a black pigmented injection molding grade) and FLX40-HP (blow molding grade). For FLE-LP an injection molded part with a thickness of 2mm was cut into a disk. For FLX40-HP a 2mm flat part of a blow molded tank was cut into a disk. The experimental blister procedure and ranking protocol was identical to the one described above for the other polyamide materials. In Figure 2, the results are shown.

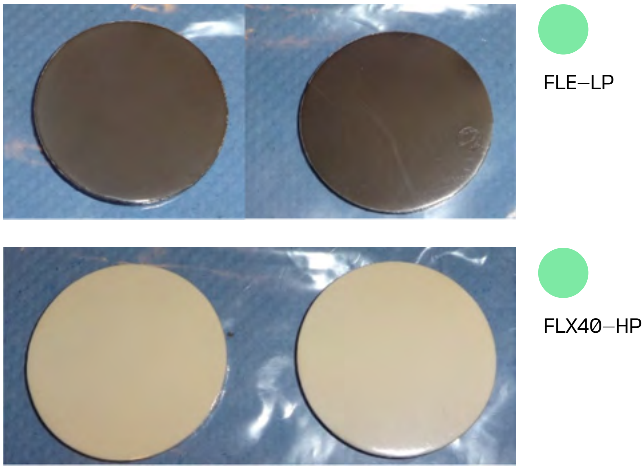

Figure 2
Blister performance of impact modified PA6 grades FLE-LP and FLX40-HP as visualized by photographs of samples and color code (for color code see text).

Blister performance of PA6 is superior, blister free, compared to HDPE & PA11 that are both blister sensitive.

Both impact modified grades are ranked blister free. Based on mechanical arguments, one would expect that impact modification of PA6 leads to a decrease of the blister resistance compared to PA6 since the modulus is decreased (see table 2) and the yield strength will be lowered (not quantified). One could also argue that potential crack propagation leading to larger scale blisters is facilitated by the presence of PA/rubber interface. In view of the olefinic and highly amorphous nature of the impact modifier, one also expects an increase of the local hydrogen supply to a growing blister since overall hydrogen diffusion and solubility will increase upon rubber modification. The experimental results however show that under the given experimental blister testing conditions, the impact modified grades are still blister proof, suggesting that the mechanical and diffusion/solubility deviations compared to PA6 are still too small to trigger blistering.

In conclusion, the blister performance of PA6 (blister free) is superior compared to HDPE and PA11 (both materials are blister sensitive) in a rather severe experimental blister test. These blister results are rationalized by local hydrogen diffusion, solubility and mechanical arguments. Impact modification of PA6 still leads to superior blister free performance.

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