

IMPROVED CFRP HYDROGEN TANK PERFORMANCE WITH GRAPHENE OXIDE MATERIALS

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Abstract: *One of the main challenges for linerless, fully composite hydrogen tank structures is the permeability of the material for hydrogen gas (H₂). In this study, a carbon fibre reinforced epoxy composite was modified with graphene oxide (GO) to decrease the H₂ permeation through the laminate with different GO concentrations. The geometric pore size of graphene is small compared to the diameter of hydrogen molecules, and therefore, it is an efficient barrier material. The permeability was tested at 20 °C and 200 bar pressure. Further, the mechanical performance of the CFRP laminates with and without GO modification was evaluated by short-beam and three-point flexural tests.*

Keywords: Carbon fibres; Energy Materials; Nanoparticles; Adhesion; Permeability

1. Introduction

The transition towards more sustainable options in transportation has evoked an interest in lightweight, high-pressure vessel options for hydrogen storage. Especially linerless fully composite hydrogen tank structures are in the interest of the automotive industry. The main challenge of these structures is the permeability of the material for small molecule hydrogen gas.

Incorporation of impermeable fillers, such as graphene oxide (GO) and reduced graphene oxide (rGO), can effectively decrease the hydrogen permeability of polymeric materials [1]. The oxygen-containing functional groups in GO act as spacers between graphene layers and trap the H₂ molecules on the graphene sheets with hydrogen bonds [1]. Also, topological defects developed during the GO synthesis are shown to enhance the H₂ storage capacity of GO [1]. Reduced graphene oxide (rGO) has fewer oxygen groups in its structure compared to GO. Rajaura et al. [1] reported better H₂ uptake capacity (1.9 wt%) for GO compared to rGO (1.34 wt%) at room temperature and 80 bar pressure. Singh et al. [2] reported hydrogen uptake of 3.12 wt% at -196 °C and 30 bar pressure for thermally (300 °C) exfoliated GO flakes. Regardless of extensive studies on the H₂ permeability of GO and rGO sheets and laminates, their application to fibre reinforced hydrogen tank structures is not yet covered. Graphene is considered one of the most effective reinforcement materials for polymers. Significant improvements in mechanical properties (stiffness, strength, ductility) have been shown for GO/polymer nanocomposites, especially with low load [3]. Therefore, finding a synergy between the optimal mechanical performance and hydrogen storage capability of GO modified fibre reinforced pressure vessels is desirable.

In this study, the hydrogen permeability of carbon fibre reinforced epoxy (CFRP) composites with GO nanofillers was investigated by custom-made equipment. The dispersion quality of GO

in epoxy resin was studied based on optical image analysis. The effect of nanofillers on the viscosity of epoxy resin was analysed by the rheology method. The mechanical performance of composites was assessed based on quasi-static flexural testing.

2. Materials and Methods

The fibre reinforcement in this study was twill 2/2 woven carbon fibre fabrics (Primetex[®] Hexel, purchased from Kevra Oy, Vantaa, Finland) with an areal density of 200 g/m² and 0.2 mm in thickness. Standard bisphenol-A epoxy resin and suitable hardener were used as the polymer matrix system with a 26 wt% hardener to resin ratio, according to supplier's guidelines.

A stable graphene oxide-acetone slurry (10 gr GO/390 mL water/600 mL acetone) was provided by Graphenea (Donostia, Gipuzkoa, Spain). The datasheet provided by the manufacturer reported the GO particles size of 29-33 μm (90th percentile), 14-17 μm (50th percentile), and 6-7 μm (10th percentile). The X-ray photoelectron spectroscopy results provided in the datasheet suggested an elemental composition of 49-50% carbon, 41-50% oxygen, 2-3% sulfur, 0-2% nitrogen, and 1-2% hydrogen for the GO. Three types of epoxy-GO dispersions with GO concentrations of 0.038 wt%, 0.075 wt%, and 0.15 wt% were prepared to find the best combination between hydrogen-barrier properties and mechanical performance of carbon fibre epoxy composites. The GO slurry was dispersed in epoxy resin and stirred for 10 minutes by a mechanical stirrer. The GO-epoxy dispersion was placed in a vacuum oven (40°C, 0.7 bar) for 24 hours to remove acetone and water before mixing it with the hardener. Viscosities of the GO-epoxy dispersions were measured with a rotational rheometer (model MCR 301, Anton Paar GmbH, Graz, Austria) at a constant temperature of 22 °C. Shear rates between 0.1 – 100 s⁻¹ were tested using a concentric cylinder system.

The GO dispersion in epoxy was studied with an optical stereomicroscope (model MZ 7.5, LEICA, Heerbrugg, Switzerland). Epoxy resins with three different GO concentrations were cast into circular shape specimens with dimensions of 10 mm × 5 mm epoxy (diameter × thickness). The resins were first degassed in a vacuum chamber (23 °C, 0.7 bar) and then cured at 80 °C (2 hours). The areal coverage of the GO in epoxy was analysed with Image J software (1.52n version, National Institutes of Health, USA). A representative, approx. 30 mm² area was considered in the image analysis per series.

Carbon fibre reinforced epoxy composites (CFRP) were manufactured by vacuum-assisted resin infusion (23°C, 0.7 bar). The epoxy resins were degassed in a vacuum chamber before infusion. Each laminate was comprised of seven plies of twill 2/2 woven carbon fibre fabrics with ply dimensions of 200 mm × 200 mm × 0.2 mm (length × width × thickness). Composites were cured at 80 °C (2 hours) and post cured at 120 °C (4 hours) in a hot press. Steel-made spacers were used to control the final thickness of composites. Composite laminates with 2 mm and 1.4 mm thickness values were prepared for hydrogen permeability and flexural testing, respectively.

The quasi-static flexural testing of CFRP composites was carried out with a universal testing machine (model 5967, Instron, MA, USA). The three-point flexural (3PF) testing of CFRP specimens with dimensions of 1.4 mm × 13 mm × 70 mm (thickness × width × length) was performed with a 30 kN load cell, 45 mm span length, and 1 mm/min crosshead movement rate following the ASTM D7264 standard guidelines. The 3PF testing was selected as the loading condition of specimens is similar to the main loading conditions in hydrogen tanks (concurrent compression and tension). Effects of the GO dispersed epoxy resins on the interlaminar shear

strength of CFRP composites were studied by short beam shear (SBS) testing according to ASTM D2344 with specimen dimensions of 1.4 mm × 2.8 mm × 20 mm (thickness × width × length). The SBS testing was performed with a 500 N load cell, span length of 5.6 mm and 1 mm/min crosshead movement rate. Specimens for the mechanical testing were cut from the CFRP laminates using a band sawing machine (model RBS904, Ryobi, Hiroshima, Japan). Specimen edges were polished to a final finish so that fibres in each ply were clearly observable.

The hydrogen permeability of CFRP laminates was studied at 20 °C and 200 bar hydrogen pressure with custom-made equipment developed by HyCentA (Graz, Austria). The CFRP laminates for the hydrogen permeability testing were water-jet cut into circular-shaped specimens with 150 mm × 2 mm (diameter × thickness) dimensions.

3. Results and discussions

3.1 GO dispersion analysis

Figure 1 shows the optical microscope images of graphene oxide (GO) dispersed epoxy resins. Based on the image analysis, the GO coverage of 0.038 wt% and 0.075 wt% samples were 54% and 71%, respectively. The optical microscopy images of the 0.15 wt% samples were fully black, so the coverage was considered to be 100%. It is clear that already very low GO concentrations ensure good coverage, and an improvement in barrier properties can be achieved.

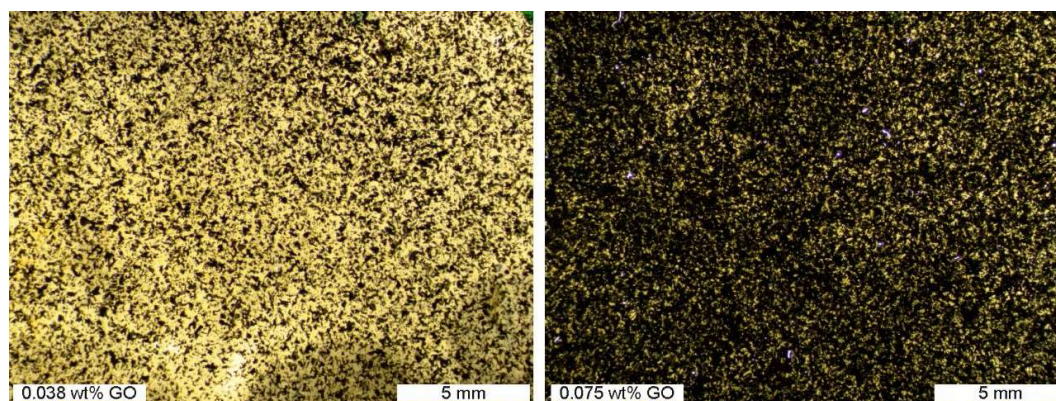


Figure 1. Epoxy films (thickness 5 mm) modified with 0.038 wt% and 0.075 wt% GO.

3.2 Rheological studies

To ensure the processability of the GO modified resin, its viscosity should not exceed the values of unmodified resin around the shear rates realistic for filament winding, which is the manufacturing method used for composite tanks. Figure 2 presents the shear rate – viscosity relation of the uncured reference epoxy and 0.15 wt% GO dispersed epoxy. The reference material obeys an expected Newtonian behaviour while the GO dispersed material shows clear shear thinning behaviour which likely evens out into a Newtonian plateau at high shear rates. This phenomenon is known as the apparent yield stress, and it represents the change in dominance from particle interactions to hydrodynamics in the flow behaviour. The lower Newtonian plateau is likely due to the small platelet-like GO particles orienting in the flow direction. Based on the results, the GO addition does not cause issues from the processability point of view, even at the highest GO concentration.

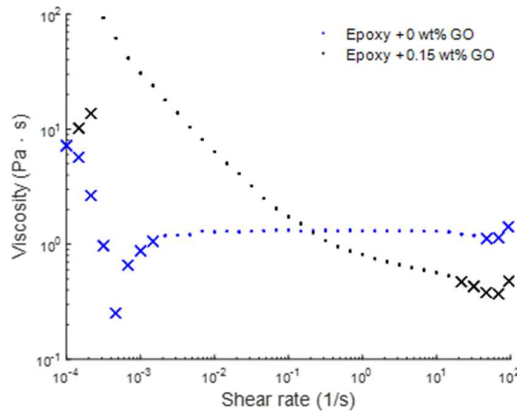


Figure 2. Viscosity- shear rate relations of pure and 0.15 wt% GO dispersed epoxy resins. Crossed out data points indicate unstable measurements within the shear rate range.

3.3 Three-point flexural (3PF) testing of composites

In Figure 3, the typical flexural stress-strain curves of CFRP composites are presented. The chord moduli (E_f^{chord}) of elasticity (within 0.001-0.003 nominal strain range) were in the range of 54 GPa for all CFRP composites. The extent of the resin cure can alter the elastic modulus of composites [4]. Similar E_f^{chord} values of the composites (see Table 1) indicate that the addition of the GO slurry does not hinder the curing state of the epoxy resin. The flexural failure strength (σ_f) values of the reference CFRP composite and CFRP composites with GO concentrations of 0.038 wt% and 0.075 wt% were in the same range considering their error margin. However, the highest GO concentration (0.15 wt%) decreased the σ_f of CFRP composites by 17%, possibly due to the GO agglomeration and stress concentration. Therefore, from the mechanical behaviour point of view, the optimal GO concentration would be below 0.15 wt%.

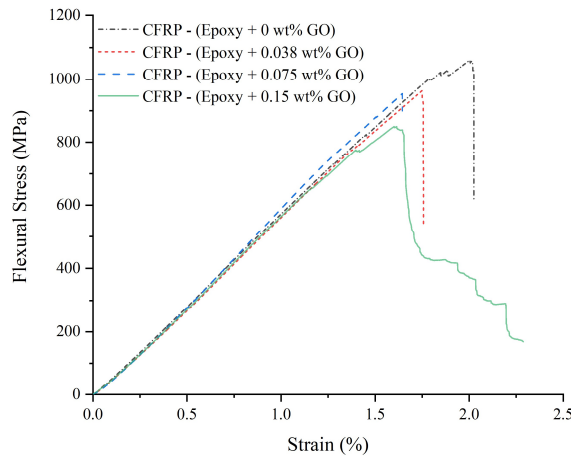


Figure 3. Typical and representative flexural stress-strain curves of CFRP composites.

The GO-dispersed composites had relatively low flexural failure strain values compared to the reference CFRP. However, the highest GO concentration (0.15 wt%) altered the brittle failure of CFRP composites to a progressive failure mode which can be ascribed to a lower interlaminar shear strength (ILSS), allowing interlaminar crack propagation before fracture.

Table 1: Results of three-point flexural (3PF) testing of the CFRP composites.

| CFRP | E_f^{chord} (GPa) | σ_f [MPa] | ε [%] |
|--------------|---------------------|------------------|-------------------|
| Referene | 54 ± 2 | 1000 ± 70 | 2.02 ± 0.07 |
| 0.038 wt% GO | 54 ± 1 | 950 ± 20 | 1.75 ± 0.09 |
| 0.075 wt% GO | 55 ± 1 | 970 ± 70 | 1.64 ± 0.09 |
| 0.15 wt% GO | 54 ± 1 | 830 ± 50 | 2.28 ± 0.08 |

3.4 Short-beam shear (SBS) testing of composites

The results of SBS testing of CFRP composites are summarised in Figure 4. The interlaminar shear strength (ILSS) of CFRP composites with 0.038 wt% GO (52 ± 5 MPa) was the same as the reference specimens (53 ± 4 MPa). Further increasing the GO content by one and two folds, respectively, decreases the ILSS values by 11% and 23% compared to the reference CFRP. Lower ILSS values of CFRP composites with GO dispersed content beyond 0.038 wt% GO can be related to the stick-slip friction between GO and epoxy and interfacial sliding inside the GO platelets. For instance, Lu et al. [5] showed that laminated polyurethane (PU) nanocomposites with 0.08 wt% GO possess a 94% higher damping factor in dynamic mechanical analysis than unmodified PU. Similarly, epoxy resins with 0.075 wt% and 0.15 wt% GO concentrations in this study might enhance CFRP composites' damping performance and long-term service life, which needs further studies with dynamic loading conditions.

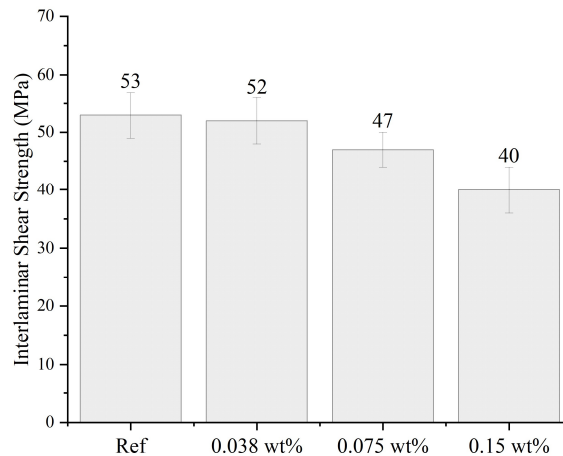


Figure 4. The average ILSS values of CFRP composites.

3.5 Hydrogen permeability

The H₂ permeability of the reference and GO modified (0.038 wt%) laminates was approximately $5 \cdot 10^{-14} \frac{mol}{cm \cdot s \cdot bar}$. Testing of composite specimens with the high pressure test system was challenging due to the relatively thick laminate (2 mm) and a good time-lag curve was not achieved during the measurement. Further, one of the sample surfaces was rough due to the peel ply used during infusion. To avoid H₂ leaking due the rough surface, an additional soft sealing was used. However, the poor time-lag curve was still an issue. Therefore, thinner

laminates (1 mm) with very smooth surfaces will be used in the test to get more accurate results and the test system will be further developed.

4. Conclusions

Lightweight and linerless carbon fibre reinforced plastic (CFRP) composites as hydrogen storage tanks should be developed to promote sustainable vehicles and transportation. This study aimed to find a synergy between hydrogen (H₂) permeability and the outstanding mechanical performance of CFRP composites. Hydrogen impermeable graphene oxide (GO) flakes were uniformly dispersed in epoxy resin as a polymer matrix for CFRP. The microscopic analysis of GO dispersed epoxy resins showed that well-dispersed and exfoliated graphene oxide flakes at low concentrations of 0.038 wt% and 0.075 wt%, respectively provide 54% and 71% surface coverage. The GO concentration of 0.15 wt% provided a complete surface coverage. Based on the rheological investigation, the GO addition did not cause any issues from the processability point of view, even at the highest GO concentration of 0.15 wt%. Overall, the mechanical performance of unmodified and GO dispersed (0.038 wt% and 0.075 wt%) CFRP composites was in the same range. The flexural strength and interlaminar shear strength of CFRP specimens with the highest GO concentration (0.15 wt%) were respectively 17% and 23% lower than the unmodified CFRP.

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5. References

1. Rajaura RS, Srivastava S, Sharma V, Sharma PK, Lal C, Singh M, et al. Role of interlayer spacing and functional group on the hydrogen storage properties of graphene oxide and reduced graphene oxide. *Int J Hydrogen Energy*. 2016 Jun 15;41(22):9454–9461. Available from: <https://doi.org/10.1016/j.ijhydene.2016.04.115>.
2. Singh SB, De M. Thermally exfoliated graphene oxide for hydrogen storage. *Mater Chem Phys*. 2020 Jan 1;239:122102. Available from: <https://doi.org/10.1016/j.matchemphys.2019.122102>.
3. Wan C, Chen B. Reinforcement and interphase of polymer/graphene oxide nanocomposites. *J. Mater. Chem*. 2012 Jan 19;22 (8):3637-3646. Available from: <http://dx.doi.org/10.1039/C2JM15062J>.

4. Bilge K, Yorulmaz Y, Javanshour F, Ürkmez A, Yılmaz B, Şimşek E, et al. Synergistic role of in-situ crosslinkable electrospun nanofiber/epoxy nanocomposite interlayers for superior laminated composites. *Compos Sci Technol*. 2017 Oct 20;151:310-316. Available from: <https://doi.org/10.1016/j.compscitech.2017.08.029>.
5. Lu W, Qin F, Wang Y, Luo Y, Wang H, Scarpa F, et al. Engineering Graphene Wrinkles for Large Enhancement of Interlaminar Friction Enabled Damping Capability. *ACS Appl Mater Interfaces*. 2019 Aug 21;11(33):30278–89. Available from: <https://pubs.acs.org/doi/full/10.1021/acsami.9b09393>.