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INFLUENCE OF FIBER/MATRIX INTERFACE ON GAS PERMEABILITY PROPERTIES OF CF/TP COMPOSITES

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Abstract: *One of the main properties to be satisfied in hydrogen applications is low gas permeability. In composite materials, this property depends on the processing parameters and in particular on the residual porosity, but also on the quality of the fiber/matrix interface. This is particularly the case in composites involving a thermoplastic matrix with carbon fibers as the lack of reactive group on the fiber surface can limit the level of interfacial interaction between the reinforcement and the matrix. In this study, the role of the interface is therefore analyzed through the investigation of the hydrogen permeability of CF/PVDF and CF/PPS composites manufactured with different grades of polymers and reinforcements. The hydrogen permeability of the composites was determined, and a correlation with the crystallization behavior of the matrix on the fiber surface could be identified. Hydrogen permeation decreases when the fiber favors matrix nucleation.*

Keywords: Composite ; Thermoplastic ; Permeability ; Fiber/matrix interface ; Hydrogen.

1. Introduction

The energy transition is seeing the development of numerous applications based on hydrogen, which has been identified as a necessity for reducing greenhouse gas emissions. Many technologies have been developed or are still being developed in this way, whether for the production, storage or use of hydrogen. In particular, new designs of hydrogen storage tanks are explored with the aim at obtaining durable lightweight solutions for transport applications.

Composite materials are suitable candidates for tank application as they combine lightness, corrosion and mechanical resistance adapted to high pressure hydrogen storage. However, the permeability of composite materials to gases [1] and in particular to hydrogen which is a light gas with a small molecular size [2] still needs to be better understood. Indeed, although the literature reports that gas permeability properties are retained for thermoset matrix composites [3], indicating good control of the fiber/matrix interface, very little data on thermoplastic matrix composites is available.

Thermoplastics (TP) have intrinsically good gas impermeability properties, of the order of $10^{-10} \text{ mol.m}^{-1}.\text{s}^{-1}.\text{MPa}^{-1}$, close to thermosets [3,4]. On the other hand, carbon and glass reinforcements also exhibit low permeability [5]. Studying hydrogen permeation in thermoplastic composites therefore consists in investigating the role of the interface on this property.

Interface issues are well known in composites. Reinforcements are generally sized before forming to improve mechanical strength but also to ensure good adhesion with the resin. Regarding hydrogen permeability, adhesion is however not necessarily the key criteria and this study therefore proposes an in-depth analysis of the interfacial interactions in thermoplastic composites and its influence on hydrogen permeability.

To do so, the behavior of carbon fiber reinforced composites manufactured with matrices of different nature was investigated. Poly(Vinylidene Fluoride) (PVDF) was first chosen for its good intrinsic gas permeability [5]. PVDF is a fluorinated semi-crystalline polymer known for its excellent chemical resistance, dielectric properties, excellent UV and moisture resistance, low coefficient of friction and very good thermal stability between -40°C and 150°C [6]. PVDF is therefore particularly suitable for use in fluid storage and transport applications (piping), in membranes for the medical field or in piezoelectric applications [7]. However, because of the high electronegativity of the fluorine element, this polymer exhibits poor chemical interaction with its environment which limits bond formation with carbon fibers in composite applications.

For comparison purpose, Poly(Phenylene Sulfide) (PPS) was selected as this thermostable thermoplastic has a hydrogen permeability of the same order of magnitude as PVDF [4]. This semi-crystalline thermoplastic polymer is widely used in composites for its high mechanical performance, high temperature stability, fire resistance and high chemical resistance [8] and has a better compatibility with carbon fibers.

PVDF and PPS polymers and their respective CF composites are studied and compared. After checking the impregnation quality, the hydrogen permeability properties are measured to highlight the influence of the fiber/matrix interface, through different fiber/matrix pairs. Morphological and crystallization analysis at the interface were then used so as to identify the main factors that control the hydrogen permeability.

2. Experimental

2.1 Materials

In order to compare the influence of the fiber/matrix interface on the gas permeability properties, two grades of PVDF were characterized and used for the manufacture of composite. The polymers used were in the form of 100 µm thick films. The first grade is a homopolymer PVDF (PVDF-H) while the second grade is a grafted PVDF (PVDF-G) which grafted function improves the chemical affinity of PVDF. Studies on similar grafted-PVDF show a decrease in the contact angle of PVDF on carbon fibers, leading to an improvement in wettability as well as an improvement in interlaminar shear strength, indicating an improvement in the quality of the CF/PVDF interface [9,10]. The gas permeability behavior of PVDF was compared to that of PPS, used as a 50 µm film.

Composite plates were manufactured with the different thermoplastic polymers, in combination with two different carbon reinforcements in the form of a mat with a weight of 465 g/m². The reinforcement (CF-A) is an unsized reinforcement while the reinforcement (CF-B) has been treated to modify the surface of the carbon fiber. The surface activation treatment modified the chemistry of the surface and therefore induced a different interfacial interaction with the semi-crystalline polymers.

2.2 Composite manufacturing

The panels were manufactured by thermocompression molding using the film stacking method. The film stacking method consists of heating and compressing a stack of alternating layers of polymer film and dry reinforcement. The conventional thermo-compression processing cycle first consisted in a low-load heat-up phase. The reinforcement/matrix system was then loaded

when the matrix temperature was beyond its melting point in order to promote polymer flow within the fiber reinforcement. The composite was finally cooled under pressure to set the structure of the impregnated composite and demolded when the temperature decreased below 50°C.

2.3 Characterization

Void content

The impregnation quality of composite panels was characterized by the presence or absence of porosity within the manufactured material. Samples taken from the plates in identical locations were polished with silicon carbide abrasive paper and then observed under an optical microscope. The image analysis technique was then used to determine the size and distribution of the porosities in the volume of the samples and the residual void content.

Hydrogen permeability

The hydrogen permeability properties of the plates were measured by the pressure differential method using a homemade equipment. A hydrogen overpressure p_{H_2} of 1 bar was applied on one side of the composite panel. The amount of hydrogen Q in ppm that had passed through the panel of area A and thickness e during time t was measured on the other side. The permeability P_e coefficient [$\text{mol.m}^{-1}.\text{s}^{-1}.\text{MPa}^{-1}$] was then calculated under standard temperature and pressure conditions, from equation 1:

$$P_e = \frac{Q e}{t A p_{H_2}} \quad (1)$$

Cryo-fractured samples

Cryo-fractures were performed on the composite samples for analyzing the fiber-matrix adhesion. The samples were immersed in liquid nitrogen for 3 min and broken with tweezers. The low temperature of the sample allowed preventing plastic deformation during fracture. The fibre/matrix interface of the samples was then platinum coated and observed under a scanning electron microscope (SEM) in secondary electrons mode.

Differential Scanning Calorimetry

DSC measurements were carried out with a Perkin Elmer 8500 DSC equipment to determine the melting temperatures and enthalpies of fusion of the polymers and composite matrices. Sealed aluminum sample pans were prepared with 15 to 20 mg of polymer and composite. The samples were then heated from 50°C to 220°C in the case of PVDF and from 50°C to 330°C in the case of PPS, at 10°C/min. The melting temperature was recorded at the maximum of the heat flow peak, and the degrees of crystallinity of the polymers and composites were calculated from equation 2:

$$X_c = \left(\frac{\Delta H_m}{\chi_m \times \Delta H_m^0} \right) \times 100 \quad (2)$$

In equation 2, χ_m and ΔH_m are the mass fractions (equal to 100% in the case of pure polymer) and the enthalpy of fusion of the polymer, respectively. ΔH_m^0 is the enthalpy of fusion of a pure polymer crystal, which is 104.6 J/g for PVDF [11] and 76.5 J/g for PPS [12].

Polarized Optical Microscopy (POM)

Isothermal crystallization from the molten state was finally studied using Polarized Optical Microscopy (POM) by means of a Linkam THMS-600P hot stage. Thin samples containing single carbon filaments were first prepared by thermocompression molding with two polymer films (PVDF and PPS) and carbon fibers taken from the reinforcements. The material systems were heated to 200°C and 295°C for PVDF and PPS respectively over short times to avoid degradation, and pressed to obtain samples with a thickness of between 40 and 50 µm.

The crystallization study under hot stage was achieved from the molten state by first heating the polymers to temperatures of 220°C and 320°C for PVDF and PPS respectively. The samples were held at this temperature for 3 min to remove the thermal history. The samples were then cooled at a rate of 50°C/min to the set crystallization temperature (160°C for PVDF and 260°C for PPS). The direct observation of spherulitic growth during polymer crystallization under polarized optical microscope allowed identifying the bulk nucleation density and fiber-induced nucleation density.

3. Results and discussion

3.1 Impregnation quality

The plates manufactured by thermocompression using the film stacking method exhibited a low residual porosity rate (figure 1.a), and of the same order for all materials. Microscopic observations (figure 1.b) confirmed the good impregnation quality of the composite panels with no visible porosity. The differences in the hydrogen permeability behavior of the composite panels can not therefore be explained by the impregnation step as such and the presence of a different porosity level.

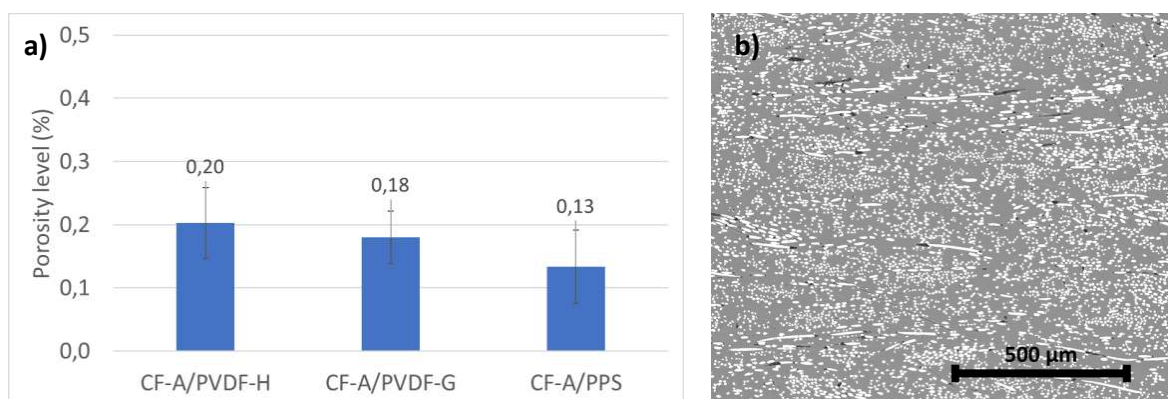


Figure 1. a) Residual porosity level in the composites and b) Microscopic observation of the CF-A/PPS composite.

3.2 Gas permeability

Figure 2 presents the hydrogen permeability measurements of the pure polymers (PVDF-H, PVDF-G and PPS) and their respective composites with the two carbon fiber references CF-A and CF-B. The pure polymers have a low hydrogen permeability in accordance with data from literature. The results also show that PVDF has a slightly lower permeability than PPS which confirms the renewed interest in PVDF for hydrogen applications.

After coupling the polymers with the carbon reinforcement, the composites show a strong increase in hydrogen permeability of several orders of magnitude. As shown previously, this result can not be attributed to an effect of the void content since all composite panels were showing a high impregnation quality. The differences in gas permeability behavior are therefore related to the quality of the fiber/matrix interface.

It should be noted that the CF-A/PVDF-G composite has a slightly lower hydrogen permeability than the CF-A/PVDF-H composite. The addition of the grafted functions improved the quality of the fiber/matrix interface [10].

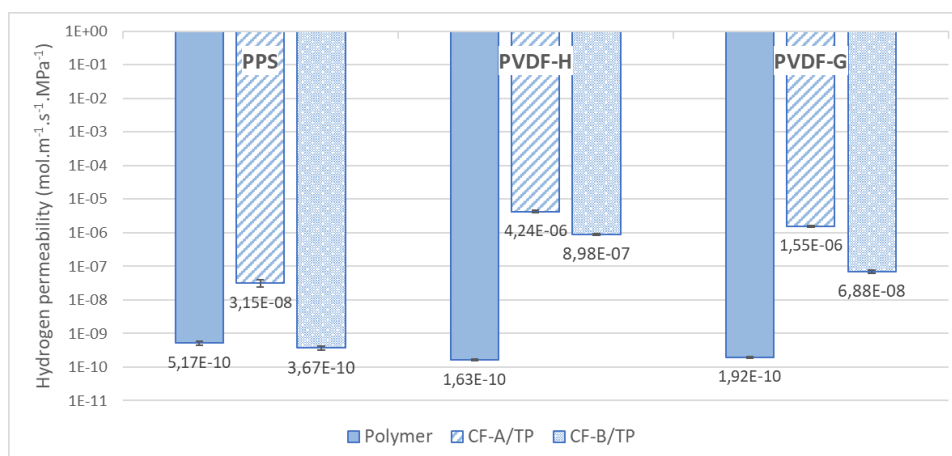


Figure 2. Hydrogen permeability of polymers (PVDF-H, PVDF-MAH and PPS) and their composites with CF-A and CF-B reinforcements, respectively.

These observations are confirmed by the hydrogen permeability measurements performed on the CF-B/PVDF-H, CF-B/PVDF-MAH and CF-B/PPS composites (figure 2). These composites, involving the activated reinforcement, show a lower hydrogen permeability than in the case of CF-A reinforcement. The functions created on the surface of the fibers during the treatment improved the quality of the fiber/matrix interface [10], leading to improved gas permeability properties of the composites. However, figure 2 shows a different behavior according to the fiber/matrix pairs. The coupled effect of the grafted functions in PVDF with the activated reinforcement improves the gas permeability properties of the CF/PVDF composites. However, the hydrogen permeability measurements remain lower than those of the CF-B/PPS composite, highlighting the influence of the fiber/matrix interface on the hydrogen permeability.

3.3 Fiber/matrix adhesion

As shown in figure 3, the SEM observations of the fractured surfaces all show poor quality interfaces. First, the presence of numerous cavities indicates that many fibers were pulled out of the matrix during the fracture. Then, little or no polymer residue can be observed on the fiber surface, indicating poor adhesion of the polymer to the carbon fibers.

The surface observation of the fiber/matrix interfaces does not allow clearly differentiating the samples. Therefore, differences in hydrogen permeability can not be correlated to different fiber-matrix adhesion levels in the composites. Nevertheless, the very high cooling rate associated with the liquid nitrogen treatment can have damaged the fiber/matrix interface. Indeed, because of the different thermal expansion coefficients of the matrix and reinforcement, the stress induced to the fiber-matrix interface upon cooling may have damaged

the interface before cryo-fracture leading to cryo-fractures that are not representative of the actual interface. Observations of fractured surfaces generated at very high speed (Charpy test) could better reveal the actual adhesion at the interface.

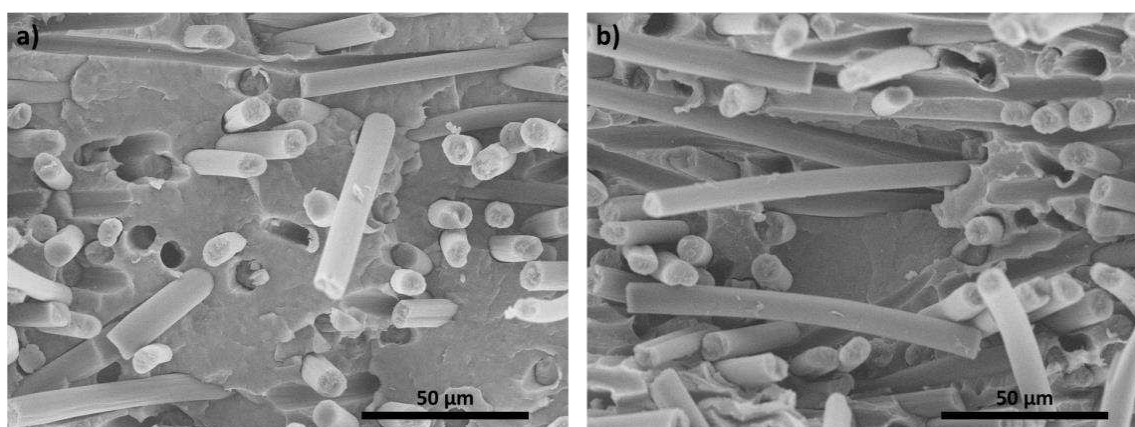


Figure 3. SEM observation of cryo-fractures of composites a) CF-A/PVDF-H and b) CF-B/PPS.

3.4 Influence of fibers on crystallization

The good adhesion of the matrix with the fiber is a source of improvement of the gas permeability as it may limit the gas paths in the interphase between the fiber and the matrix. However, this condition is necessary but not sufficient. Indeed, Monson *et al.* [13] showed in their study that a higher proportion of crystalline phase led to an improvement in gas permeability properties. As in the case of fillers, crystalline phases increase the effective path length of gases through the composites.

During the manufacturing process, the composite panels were cooled at a cooling rate of about 10°C/min. Such cooling rates have little effect on the crystallization of PVDF-H, PVDF-G, PPS and their respective composites. As shown in figure 4, the degrees of crystallinity of the polymers and the corresponding composites are of the same order of magnitude. The differences in crystallinity in the volume do not explain the differences in permeability behavior.

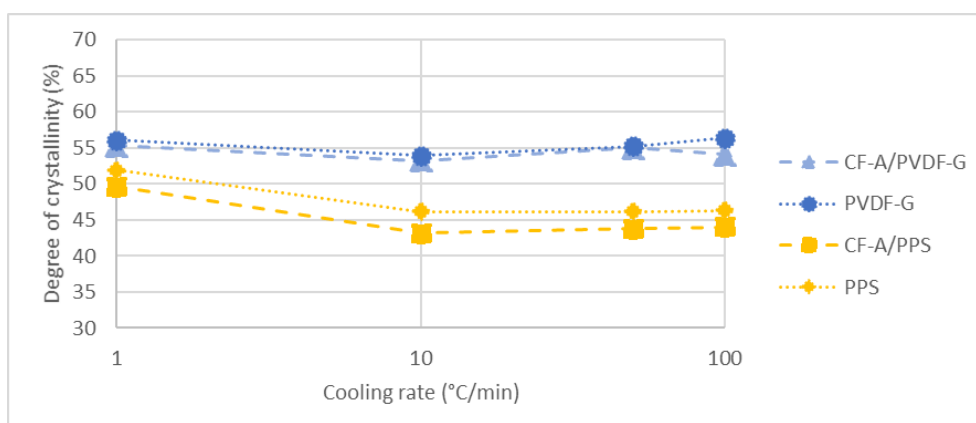


Figure 4. Degree of crystallinity of polymers and composites from DSC measurements.

In order to highlight the effect of fibers on crystallization, numerous images were taken during the spherulite growth process and the surface of the image covered with spherulites was monitored by using image analysis method. The influence of fibers was assessed by measuring the percentage of the image covered by spherulites in an area close to the fiber. In the present case, a distance of 25 μm around the fiber was considered (figure 5.a) for defining this area. The same percentage was calculated in the rest of the image, *i.e.* in an area far from the fiber, therefore representing the bulk crystallization process. The ratio between the two percentages was then used as an indicator of the influence of the fiber, a value close to unity demonstrating an absence of fiber influence on the crystallization process.

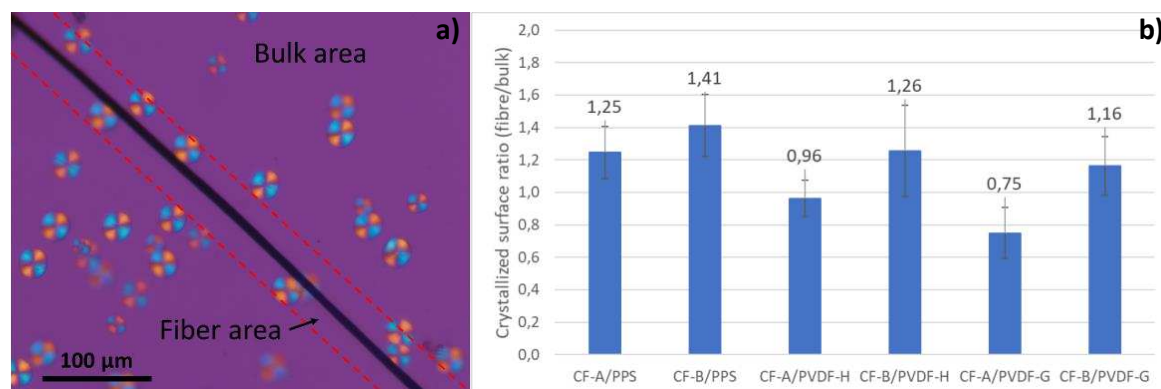


Figure 5. Influence of the fiber zone on the crystallized surface for different combinations of reinforcements and matrices. (a) Observation of growing spherulites by optical microscopy; (b) Ratio between the surface of the micrographs covered by spherulites in the fiber area and in the bulk area.

According to figure 5.b, the CF-A reinforcement has a low influence on the crystallization of PVDF and even a negative effect of the fiber, as shown by ratios lower than unity. On the other hand, the presence of the fibers impacts the crystallization of PPS, possibly through a greater nucleation effect on the fiber surface. This results in a stronger loss of permeability properties in the case of PVDF composite than for PPS composite.

By adding CF-B, the activated surface of the carbon fiber increases the ratio, indicating a higher influence of the carbon surface on crystallinity that can be correlated with the improvement of the hydrogen impermeability of the composites. The higher ratio can be due to a higher nucleating effect of the activated carbon fiber that may induce a densification of the interface [13] therefore locally reducing the hydrogen permeability.

The benefit of using a grafted PVDF appears to be very low on crystallization, although it significantly improves the permeability property of the composite when combined with CF-B (one order of magnitude difference). This suggests that other phenomena also influence the permeability property at the fiber/matrix interface, adhesion being one of the parameters to be considered.

4. Conclusion

This study demonstrates the influence of fiber/matrix interface in carbon fiber reinforced thermoplastic composites on the hydrogen permeability properties. In particular, the nucleating effect of the fiber surface appears as a key factor for improving the permeability property, most likely because of an interphase densification at the fiber-matrix interface. The combination of a grafted polymer with an activated reinforcement allows to significantly decrease the hydrogen permeability. This improvement is attributed to the better affinity of the polymer with the reinforcement. The same observation was made with PPS, which exhibit a higher affinity with the activated carbon fiber leading to a permeability property similar to that of the neat polymer.

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