THE CRYSTALLINITY DEGREE INFLUENCE ON THE WEATHER RESISTANCE OF CF/PPS COMPOSITES

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Abstract
Polyphenylene sulphide (PPS) is a semi-crystalline high-performance thermoplastic used in the aeronautic field as a composite usually reinforced with carbon fibers. The crystallinity of semi-crystalline thermoplastics can alter significantly their mechanical properties and weather resistance. In this work, carbon fiber/polyphenylene sulphide (CF/PPS) composites were processed by hot compression molding with three different crystallinity degrees. Hygrothermal, salt spray and ultraviolet radiation climatic chambers were used to evaluate the influence of the crystallinity degree on CF/PPS composites weather resistance. The thermal and mechanical properties of the processed laminates, as obtained and weathered, were investigated by differential scanning calorimetry (DSC), interlaminar shear strength (ILSS) and acoustic vibration damping tests. The results showed that the less crystalline CF/PPS samples had their crystallinity degree increased after weathering. Salts spray exposure affected the reinforcement/matrix interphase and reduced the Young's modulus. In addition, the ultraviolet radiation reduced the Young's modulus and the interlaminar shear strength due to photooxidation. The samples with higher crystalline content were more were more severely photodegradated. In conclusion, the composites with higher crystalline degree showed to be more resistant to humidity and salinity. However, those with lower crystalline degree were more resistant to the effects of the ultraviolet radiation.

1. Introduction

Polyphenylene sulphide (PPS) is a high-performance semi-crystalline thermoplastic with a glass transition temperature (T_g) of about 90°C and a melting temperature (T_m) around 285°C [1]. This polymer is used as a composite matrix in aeronautic applications due to its outstanding properties such as inherent flame resistance, high-temperature stability, good chemical resistance, anti-aging, high hardness and rigidity [2-4]. Moreover, it can be molded with high reinforcement contents due to its low melt viscosity (~200 Pa.s) [1,5].

In semi-crystalline thermoplastics, the crystallinity degree affects their mechanical properties, while the amorphous regions are more effective in absorbing impact energy, the crystalline regions have an influence on the polymer stiffness [6]. The level of crystallinity also affects their resistance to hostile environments [7]. The PPS, for example, can achieve a high crystallinity degree of about 60% [8]. The degree of crystallinity is determined by many factors, including the processing cooling rate [6].

Composite laminates with a thermoplastic matrix can be obtained by a processing technique known as hot compression molding. This processing can be achieved by placing plies of polymer and

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reinforcement into a mold cavity with a proper sequence and heating it up to a temperature higher than the thermoplastic melting point. The material needs to be kept under pressure at this temperature in order to percolate into the reinforcement plies. Finally, the material is cooled down to the room temperature to form the composite laminate [9].

In this work, carbon fiber/polyphenylene sulphide (CF/PPS) composites were processed by hot compression molding and three different crystallinity degrees were obtained by varying the cooling rate. In order to investigate the influence of the crystallinity degree on the weather resistance of CF/PPS composites, the following climatic chambers were used: hygrothermal, salt spray and ultraviolet radiation. The thermal and mechanical properties of the processed laminates, as obtained and weathered, were investigated by the following methods: differential scanning calorimetry (DSC), interlaminar shear strength (ILSS) and acoustic vibration damping.

2. Materials and Methods

2.1. Material

The CF/PPS composites were processed by hot compression using 15 layers of plain weave carbon fabric provided by Hexcel and PPS films supplied by Curbell Plastics. The laminates were obtained with dimensions of 300 x 300 x 2.5 mm and a reinforcement/matrix volume content of 60/40 (v/v).

In the processing, the material was heated up from room temperature to 315 °C at approximately 10 °C.min^{-1}, held in this temperature for 30 min under 1.2 MPa of pressure and then cooled to room temperature. Three different cooling rates were performed in order to vary the final crystallinity degree, a fast rate of about 10 °C.min^{-1}, a slow rate of approximately 1°C.min^{-1} and an air cooling, obtained by leaving the press, die and laminate cool naturally in air.

2.2. Weathering

The influence of the crystallinity degree on the weather resistance of CF/PPS composites was investigated using the following climatic chambers: hygrothermal, salt spray and ultraviolet radiation. All the samples were periodically weighed in order to monitor possible changes in weight.

The hygrothermal exposure was based on ASTM D 5229/D 5229M 04 and was performed on a controlled Marconi climatic chamber, model MA835/UR. The specimens were exposed to 80°C and 90% relative humidity atmosphere in a chamber during a period of eight weeks.

Salt spray weathering was based on ASTM B117-11 and carried out in an Equilam salt spray chamber. The specimens were exposed to a direct spray of a 5%-by-mass aqueous solution of NaCl at 35°C during three weeks.

Artificial photodegradation was carried out following the ASTM G 154 standard using an accelerated weathering tester model QUV/spray with solar eye irradiance control. The damages caused by sunlight and dew were reproduced by 8 h periodic cycles at 60°C under UV-A light and 4 h at 50°C under water condensation.

2.3. Differential scanning calorimetry (DSC)

The crystallinity degree of the composites matrix was calculated using a Seiko Exstar 6000 - DSC 6220 differential scanning calorimeter, operating under nitrogen flow at a heating rate of 10 °C.min^{-1}. They were determined according to Eq. 1:

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$$X_c(\%) = \frac{\Delta H_c}{\Delta H°_m} \times 100\% \quad (1)$$

where: X_c is the crystallinity degree, ΔH_c is obtained by the melting peak area, and $\Delta H°_m$ is the melting enthalpy of PPS 100% crystalline, taken as 80 J/g according to the literature [8].

2.4. Interlaminar shear strength (ILSS)

ILSS tests were performed according to ASTM D2344 standard using a Shimadzu autograph AG-X series precision universal machine at room temperature, constant cross-speed of 1 $mm.min^{-1}$ and a load cell of 5 kN. The dimensions of the specimens were 15 x 5.5 x 2.5 mm.

2.5. Acoustic vibration damping

The acoustic vibration damping was used to determine Young's modulus from the natural frequency. At the technique applied, a rectangular specimen under flexure mode was lightly stroked and the acoustic response captured was used to calculate the Young's modulus. The impulse excitation technique was applied using Sonelastic® equipment, developed by ATCP – Physical Engineering, at Brazil. This non-destructive test was performed according to ASTM 1876 standard, using specimens with dimension of 50 x 14 x 2.5mm.

3. Results and Discussion

The effect of the weathering on the crystallinity degree of CF/PPS composites is shown in Figure 1. A significant increase on the crystallinity was observed after hygrothermal and ultraviolet weathering for the composites obtained by fast cooling. The variation verified after the hygrothermal weathering was probably due to the high temperature (80°C) inside the hygrothermal chamber and the water ingress, which enabled the movement and reordering of the polymer chains, resulting in the crystalline increase. In contrast, when a semi-crystalline thermoplastic is exposed UV radiation it can undergo a process called chemi-crystallization, where part of the polymer chains in the amorphous region are broken, giving them enough mobility to form new crystals [10]. This could explain the crystalline increase after the UV weathering.

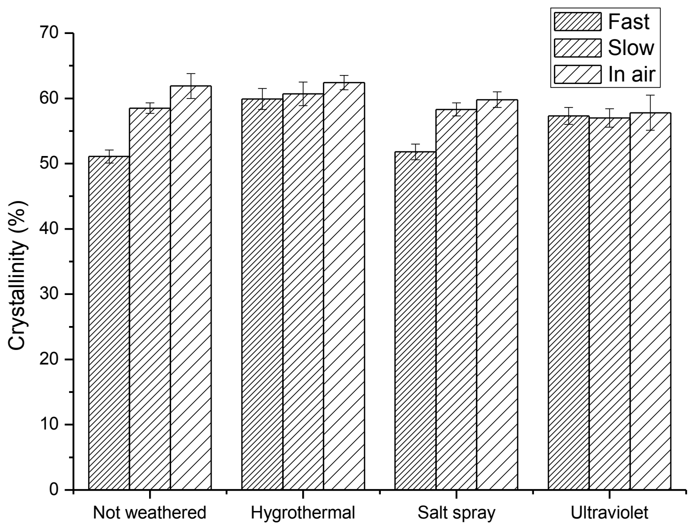

Figure 1. Crystallinity degree of the weathered CF/PPS composites.

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The Young's moduli (Figure 2) of the samples exposed to salt spray were all reduced, indicating that the addition of salt (NaCl) in the water has a significant influence on the degradation process of CF/PPS composites. Since the modulus of the hygrothermaly weathered samples were not affected. Moreover, the Young's modulus of the laminates with higher crystalline contents exposed to UV radiation was also reduced, suggesting that the samples with higher crystalline contents are more affected by UV radiation.

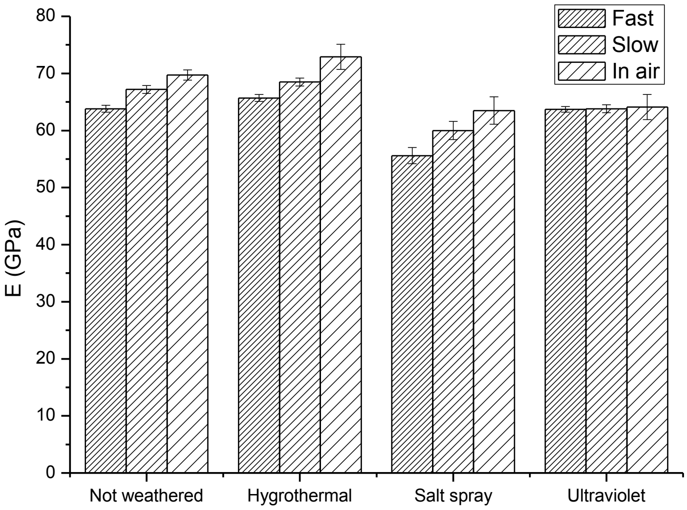

Figure 2. Young's modulus of the weathered CF/PPS composites.

Regarding the laminates tested by ILSS (Figure 3), those photodegraded exhibited an important reduction in the interlaminar shear strength, especially for the samples with higher crystalline content. The laminates weathered in the salt spray chamber, however, were severely degraded, hindering the execution of the test.

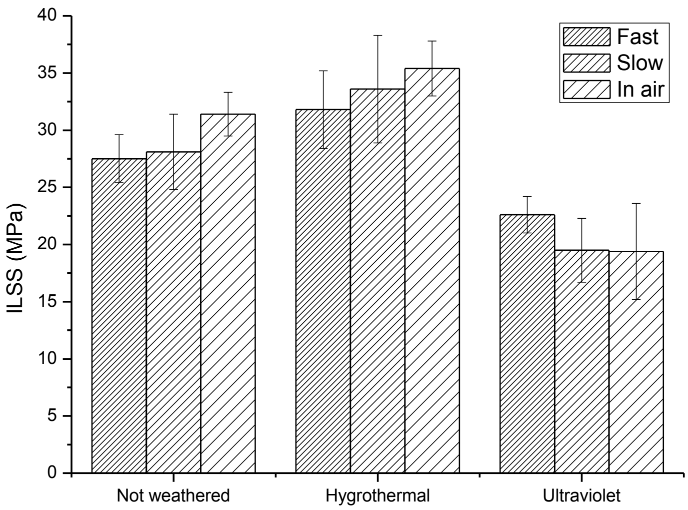

Figure 3. ILSS of the weathered CF/PPS composites.

The intensification of the photodegradation for the samples with higher crystalline contents was also possible to observe by stereoscopy, as shown in Figure 4.

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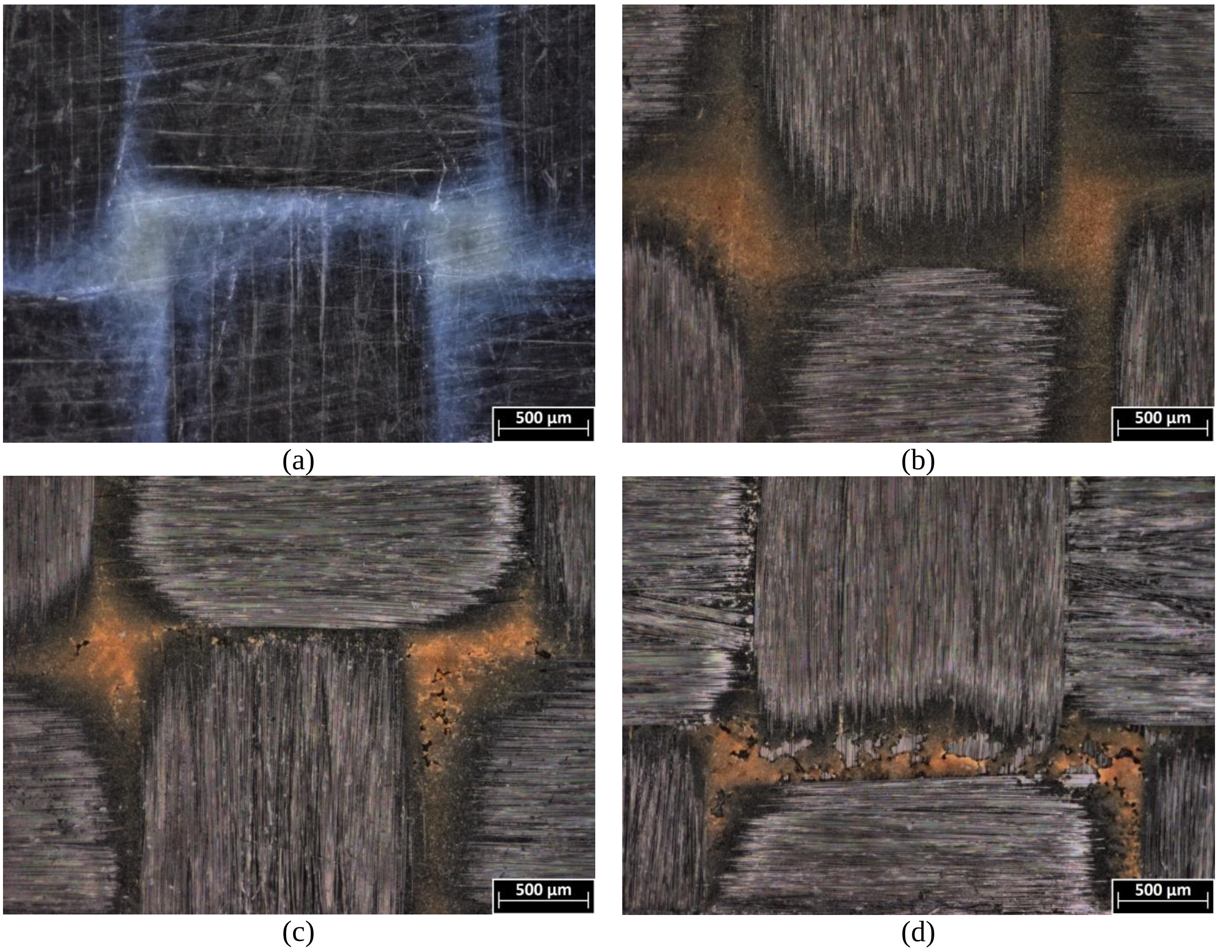

Figure 4. Stereoscopy of the UV weathered CF/PPS laminates with: (a) no weathering; (b) low crystallinity degree; (c) medium crystallinity degree; and (d) high crystallinity degree.

3. Conclusions

The water ingress and the high temperature affected the crystallinity degree of the less crystalline samples, increasing it. A similar increase in crystallinity was also observed after exposure to UV radiation; however, this variation was a result of a chemi-crystallization.

Moreover, the composites exposed to salt spray were more severely degraded when compared with the hygrothermal weathering. The salty water reduced the Young’s and degraded the CF/PPS interlaminar adhesion. In contrast, the ultraviolet radiation affected more severely the specimens with higher crystalline contents. As a result, their Young’s modulus and the interlaminar shear strength were decreased due to photooxidation.

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