LOCAL CHARACTERIZATION BY CYCLIC INDENTATION TEST OF POLYMER MATRIX IN 3D CARBON FIBER COMPOSITES

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Abstract

In this work, local mechanical properties of PR520 epoxy resin matrix in 3D carbon fiber composite (*in-situ*) have been investigated through a cyclic indentation loading method and compared with that of the neat material. This loading enables to evaluate elastic as well as time dependent response of the material. The evolution of classical indentation and cyclic behaviour parameters with time is studied. The 3D carbon fiber composite used in this study contains a number of large resin pockets among fiber bundles (mesoscopic scale) with a characteristic dimension ranging from several hunred of micrometers to several millimeters. First of all, the homogeneity of polymer matrix was verified on the surface and in the volume of the composite. Then, a statistical analysis through Student t-test of *in-situ* parameters at the mesoscopic scale was performed with comparison to the neat material. The result showed that there is at least a 95% of probability that the neat and *in-situ* data sets belong to different populations. However this difference is quite small (between 1 and 2.5%) and almost constant with cycles.

1. Introduction

The mechanical behaviour of a composite material is usually modelled with material properties measured on neat matrix and fibers separately. However, curing of polymer matrix around the fibers, as in Resin Transfer Moulding process, introduces thermal residual stresses in the material and could modify the crosslinking of polymer matrix. Cured this way matrix could demonstrate different local mechanical behaviour (*in-situ*) compared with its neat form. Since in composite materials, failure initiates at the microscopic scale, any change of mechanical properties of the constituents could be crucial for the failure prediction. One of few techniques that allows for an experimental local characterization of the matrix is the instrumented indentation. It consists in penetrating a diamond tip into the material surface and studying the evolution of the displacement as a function of the applied load during a load-unload cycle. The application of Oliver and Pharr analysis method [1] allows to calculate Hardness and Elastic modulus of the material from load displacement indentation curves. Previous work conducted on unidirectional carbon-fiber polymer-matrix composites [2] showed that the main difficulty in matrix characterization with instrumented indentation is to decouple the constraint effect of surrounding fibers from a proper change of polymer matrix properties. Two-dimensional finite element simulations of elasto-plastic composite matrix showed that, to avoid any constraint effect, the resin pockets should be at least 50 times larger than maximal penetration depth [3]. In the following, we will refer to unconstaind properties of composite matrix as *in-situ* properties measured respecting this condition and to properties of polymer without fibre reinforcement as neat properties. Very few studies are available in the literrature that aim to compare experimental local constituent neat and *in-situ* properties in composite materials. In the particular case of 997-3 epoxy resin/ carbon fiber composite system, Gregory and Spearing [3] found that *in-situ* modulus is $20-30\%$ higher than neat modulus while there was virtually no difference in the measured hardness values. Hardiman [3] found on co-cured neat and *in-situ* 6376 epoxy resin that, even for unconstrained values, the *in-situ* modulus depends on matrix pocket radius. That is probably caused by a far-field interphase effect and/or to a difference in local curing conditions near fibers. He concluded that the difference between mean values of unconstrained *in-situ* modulus and neat modulus of 6376 epoxy resin is about 10% while the difference on Hardness is about 6%. In both cases, tests were conduced on unidirectional carbon fiber reinforced composites, fabricated using an autoclave cure, in the direction parallel to fibers. Moreover, the analysis method of nanoindentation data used in previous studies provides only elastic and plastic material properties omitting viscous nature of polymer [4]. The aim of this work is to characterize *in-situ* mechanical properties of the polymer matrix of a 3D interlock carbon-fiber reinforced composite and their deviation from neat polymer by means of an instrumented indentation cyclic loading. This kind of experimental protocol allows to evaluate not only elastic and plastic, but also time dependent response of the material.

2. Material and experimental procedure

2.1. Materials

The material employed in this study is the PR520 epoxy resin ($T_g \cong 150°C$, Tensile Young's Modulus $= 4GPa$ [5]) in its pure form (neat) and as matrix of an RTM 3D interlock carbon-fiber reinforced composite (*in-situ*). The 3D composite material contains a number of large resin pockets among fiber bundles (Fig. 1) with a characteristic dimension ranging from several hunred of micrometers (in the volume) to several millimeters (on the surface). That allows to perform instrumented indentation measurements of the matrix material avoiding constraint effects of the surrounding fibers.

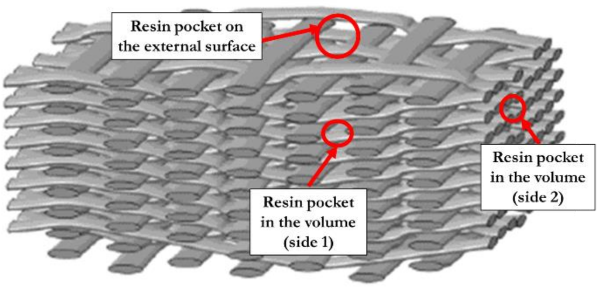

Figure 1. Scheme of the 3D interlock carbon-fiber reinforcement similar to the one used in this study [6]

In-situ tests have been perfomed in resin pockets on the external surface and in the volume of the composite sample.

2.2. Cyclic indentation test and analysis method

Both neat and *in-situ* PR520 epoxy resin have been tested using a cyclic indentation procedure on the force controlled Ultra-Micro Indenter Fischerscope H100C equipped with a diamond Vickers tip. The testing protocol (Fig. 2 a) consists in 40 load-unload cycles between a minimum force of $0.5mN$ and a peak force of $10mN$ with a loading/unloading rate of $2\ {mN}/{s}$. A hold phase at $0.1mN$ was introduced at the beginning of the test to perform thermal drift correction on the load displacement data.

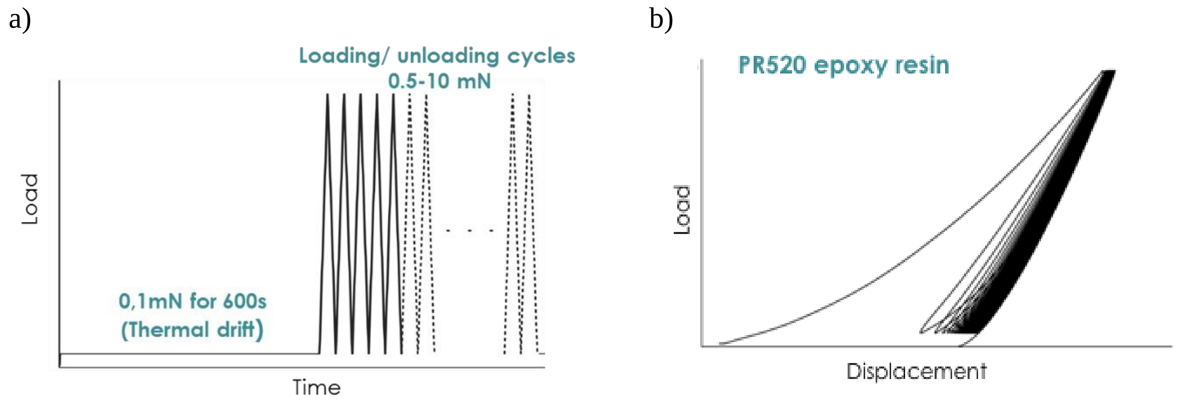

Figure 2. Cyclic indentation test protocol used in this study to evaluate time dependent indentation response of polymer and polymer matrix composite (a) and typical result of cyclic indentation test on PR520 epoxy resin (b)

The load-displacement curves obtained on the PR520 epoxy resin (Fig. 2b) are characterized by large hysteresis loops that evolve with cycles. This response suggests that a large amount of energy is dissipated in each indentation cycle and that the material behaviour is far from being purely elasto-plastic. The analysis of hysteresis loops is done through four parameters. The evolution of these parameters with time (cycles) is then traced. The first two parameters are the classical material properties extracted from indentation load displacement curves: the indentation modulus and the hardness, calculated according the Oliver and Pharr analysis method. The indentation modulus (E^*) is calculated from unload curve under the assumption of perfectly elastic unloading. The Oliver and Pharr procedure consists in evaluating the reduced modulus of the material (E_r) from its stiffness (S) and the projected area of contact (A_p) according to Eq. 1:

$$E_r = \frac{\sqrt{\pi}}{2\sqrt{A_p}} S \tag{1}$$

The stiffness S is the slope of the unload curve at the maximum load. The indentation modulus E^* is then calculated from the reduced modulus by accounting for the effect that the indenter is not perfectly rigid (Eq. 2).

$$E^* = \frac{1}{\frac{1}{E_r} - \frac{1-v_i^2}{E_i}} \tag{2}$$

Where v_i and E_i are the Poisson's ratio and Elastic modulus of the indenter. The hardness (H), is the ratio between the maximum load and the projected area of contact (Eq. 3).

$$H = \frac{P_{max}}{A_p} \tag{3}$$

Hardness (or mean contact pressure) is proportional to the yield stress in elasto-plastic material [6], like metals, and is thus related to plastic deformations. Indentation modulus and hardness are calculated according to analysis method developped for elasto-plastic material and could thus be meaningless in the case of material that exhibit time dependent behaviour. However their evaluation is useful to compare our results with that obtained in previous studies [2,3]. The last two parameters considered are releated to the cyclic behaviour : the mean displacement (h_{mean}) and irreversible part of indentation work (η). The mean displacement is calculated on each unloading curve and its evolution with time (cycles) is analogous to creep behavior and could thus be considered as related to viscoelastic and viscoplastic contributions. η represents the amount of energy dissipated during a load-unload cycle (W_{irr}) with respect to the total energy (W_{tot}) (Eq. 4):

$$\eta = \frac{W_{irr}}{W_{tot}} \tag{4}$$

In the case of elasto-plastic materials, η would not be zero only during the first load-unload cycle, in which energy is dissipated to produce plastic deformations. It has been shown that η is proportional to the ratio between hardness and elastic modulus [7]. In our case, we assume that purely plastic deformations occur only during the first load so that η at the first cycle includes energy dissipated for plastic, viscoelastic and viscoplastic deformations, while from the second cycle, it is an indicator of the viscoelastic and viscoplastic flow.

3. Results and discussion

3.1. Indentation cyclic behavior of PR520 epoxy resin

The experimental procedure described in the previous section was applied to the neat and *in-situ* PR520 epoxy resin. The evolution of indentation modulus, hardness, mean displacement and of the irreversible part of work of indentation with cycles are represented in Figure 4a, 4b, 4c and 4d respectively for neat (circles), *in-situ* measured on the volume (squares) and *in-situ* measured on the external surface (triangles) polymer. Error bars represent mean value ± one standard deviation.

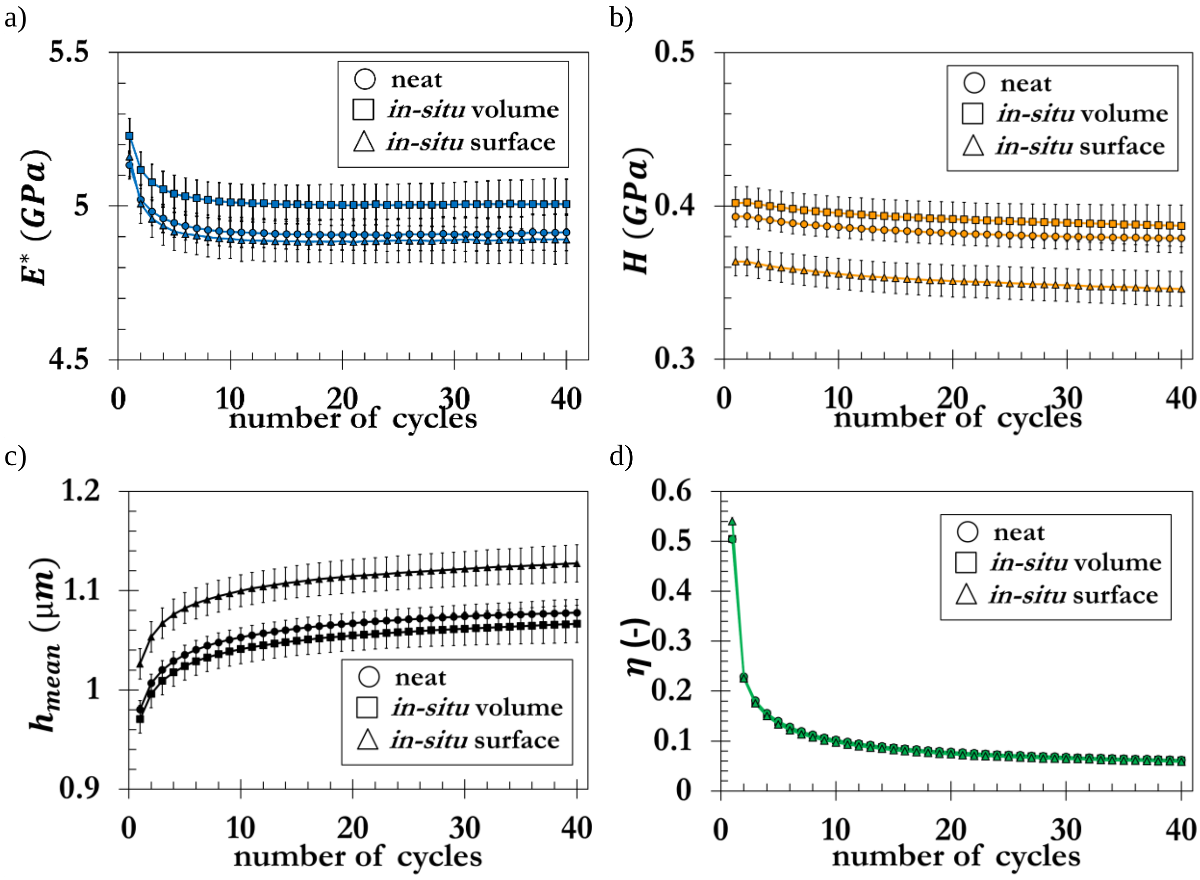

Figure 4. Evolution of indentation modulus (a), hardness (b), mean displacement (c) and work of indentation (d) with indentation cycles for the neat *(*circles), *in-situ* measured on the volume (squares) and *in-situ* measured on the external surface (triangles) PR520 epoxy resin

We can observe that the cyclic behaviour of neat and *in-situ* epoxy resin is quite similar. In particular, the indentation modulus (Fig. 4a) decreases with cycles and stabilizes after about 10 cycles to a constant value, while the hardness (Fig. 4b) is virtually constant with cycles. The mean displacement (Fig. 4c) follows an evolution with cycles (time) similar to that of displacement in indentation creep tests and η (Fig. 4d) drops quickly in the first ten cycles, then it continues to decrease and tends to a constant non-zero value. Moreover a slight difference in mean values between *in-situ* measured in the volume and *in-situ* measured on the surface and between neat and *in-situ* data sets is observed and will be discussed in the following.

3.2. Heterogeneity of polymer matrix in the composite

Cyclic indentation test protocol (Fig. 2a) has been applied on unconstrained composite matrix, which corresponds to the large resin pockets of the 3D composite. The composite manufacturing process could induce differences in local resin degree of cure because of the complex thermal paths in 3D interlock. To verify the homogeneity of polymer matrix, several tests have been performed on different resin pockets found on the external surface and in the volume of the sample (Fig. 1). In order to understand if the difference among the results is significant from a statistical point of view, the Student t-test [8] have been applied to compare the mean values of different pockets. The Student t-test consists in calculating the value of the Z parameter from the mean values (X), standard deviations (σ) and number of tests (N) of two data sets (Eq. 5):

$$Z = \frac{|X_1 - X_2|}{\sqrt{\frac{\sigma_1^2}{N_1} + \frac{\sigma_2^2}{N_2}}} \quad (5)$$

The calculated value of Z is compared to its critical value Z_{crit} found in tables [8] for the level of confidence chosen (99.9% in this case) and for the number of degree of freedom d_f (Eq. 6):

$$d_f = N_1 + N_2 - 2 \quad (6)$$

The comparison between the two values of Z allows to accept ($Z > Z_{crit}$) or to reject ($Z < Z_{crit}$) the null hypothesis that the two data sets are drawn from different populations.
The study of the homogeneity of the polymer matrix have been done at first by comparing cyclic indentation results obtained in resin pockets found in the volume of the composite sample. A total of 10 resin pockets have been tested -5 pockets on side 1 and 5 pockets on the side 2 (Fig. 1) – and 10 indentation tests have been performed in each pocket. By appling Student t-test on each pair of pockets of side 1 and side 2, we did not find any statistically significant difference on mean values for an interval of confidence of 99.9%. The same result have been obtained by comparing the average value of all pockets on side 1 with all pockets on side 2. Then, the Student t-test have been applied to compare different pockets on the surface of the sample. A total of 4 pockets have been tested and 30 indentations have been performed in each pocket. The comparaison of each pair of pockets through the Student t-test showed, even in this case, no statistically significant difference. Finally, an average of all resin pockets in the volume and an average of all resin pockets on the external surface (results presented in Fig. 4) have been compared. In this case, the Student t-test revealed that there is a 99.9% probability that the data belong to different populations. The percent difference between surface and volume data for each parameter and for all cycles is reported in Figure 5.

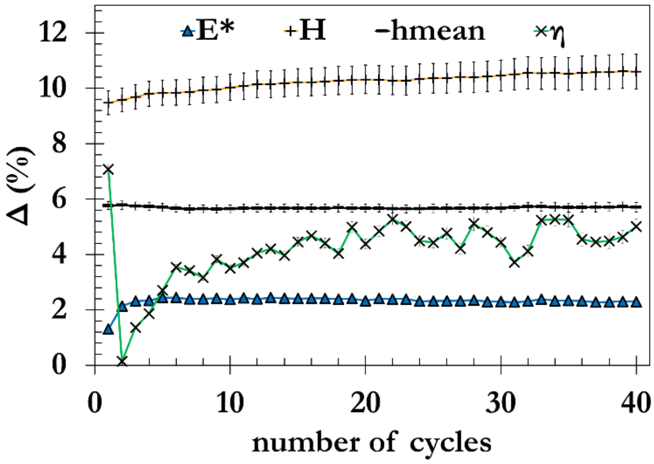

Figure 5. Evolution with cycles of the percent difference between indentation performed in the volume and on the surface of the composite of indentation modulus (Δ), hardness (+), mean displacement (-) and η (×) as a function of cycles

From Figure 5 we can observe that, except for η, the percent difference between the two data set is almost constant with cycles. This difference is about 2% on indentation modulus, 6% on mean displacement and 10% on hardness. This suggests that the skin effect observed on injected neat polymer parts is also present in the resin transfert moulded composite. To avoid the influence of the skin effect not present in polished neat polymer sample, only results obtained in the volume (45 tests) were considered for a comparison later on.

3.3. Neat vs. *in-situ* properties of PR520 epoxy resin

The evolution with cycles of indentation modulus, hardness, mean displacement and η of neat (circles) and *in-situ* in the volume (squares) PR520 epoxy resin are represented in Figure 4a, 4b, 4c and 4d respectively. As previously observed, the evolution with cycles of the different parameters is similar in the two cases. However a slight difference in mean values of the two sets of data exists. In order to understand if this difference is significant form a statistical point of view, the Student t-test have been applied. The values of Z calculated at each cycle (Eq. 5) are represented in Figure 6 as a function of the number of cycles for all the parameters. The dashed red lines represent the values of Z_{crit} for an interval of confidence of 99.9% (upper line) and 95% (lower line).

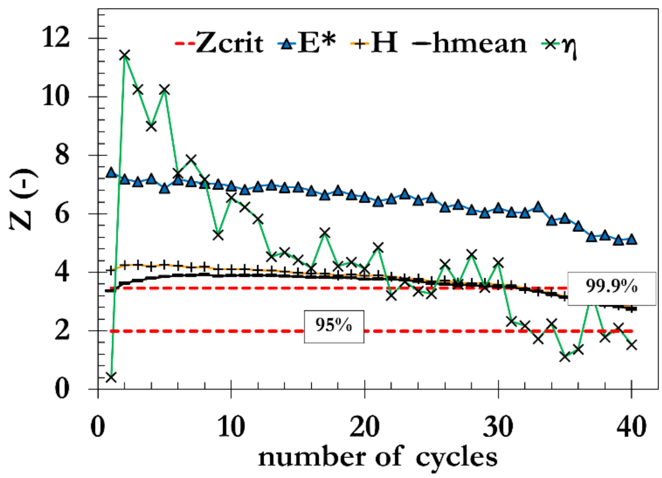

Figure 6. Evolution with cycles of the parameter Z of indentation modulus (Δ), hardness (+) mean

displacement (-) and η (×) and of Z_{crit} for an interval of confidence of 99.9% (upper line) and 95% (lower line)

The result of statistical test suggests that there is a 95% of probability that the values of the parameters measured on neat and *in-situ* resin belong to different populations. The probability is higher (99.9%) in the case of indentation modulus. The percent difference of all parameters between neat and *in-situ* mean values have been quantified and the results are reported in Figure 7.

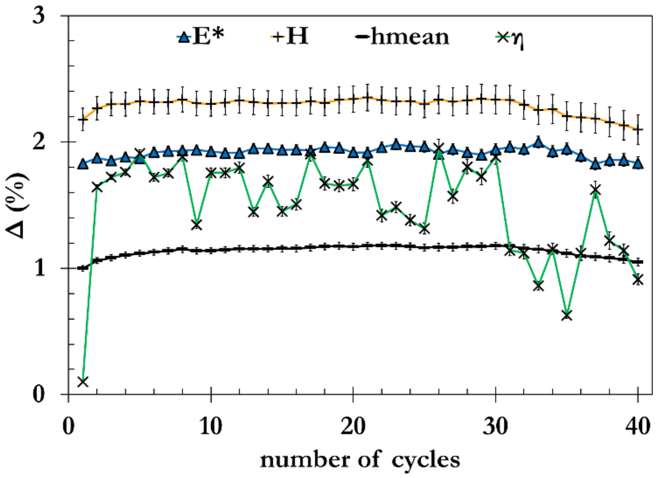

Figure 7. Percent difference between neat and *in-situ* mean values of indentation modulus (Δ), hardness (+) mean displacement (-) and η (×)

In Figure 7, we can observe that the percent difference between neat and *in-situ* mean values is quite small, that it lies between 1% and 2.5% and that it is almost constant with cycles (except for η). This result is significantly lower than that reported by [2,3], namely 10 and 20% for elastic modulus, respectively, and 6% for hardness. However, as mentioned in the introduction, Hardiman et al. [2] found that even unconstrained modulus depends on pocket size and, even if the average unconstraind modulus is 10% higher than the neat modulus, for the larger resin pockets the difference between neat and *in-situ* values is about 2% that is consistent with our result.

4. Conclusion

In this work, local mechanical properties of neat and *in-situ* PR520 epoxy resin have been investigated through a cyclic indentation loading method. This loading path enables to evaluate time dependent response of the material. The resulting force-displacement curves are characterized by large hysteresis loop that evolve with cycles. The parameters extracted from load-displacement hysteresis loops are: indentation modulus, hardness, mean displacement and the irreversible part of work of indentation (η). The 3D composite material used in this study contains a number of large resin pockets with a characteristic dimension of several hundred of micrometers allowing to measure the unconstrained properties of polymer matrix. The polymer mechanical response is found to be homogeneous in all tested pockets in volume, but a significant difference has been found between pockets in the volume and on the external surface. The indentation cyclic behaviour of neat and *in-situ* PR520 epoxy resin are quite similar, while a slight difference on mean values has been observed. In order to understand if this difference is statistically significant, the Student t-test has been applied to all parameters for all indentation cycles. The result of statistical test suggests that there is a 95% of probability that the values of the parameters for neat and *in-situ* resin are statistically different. The probability is higher (99,9%) in the case of indentation modulus. However, the percent difference is quite small (between 1 and 2,5 %) and it is virtually constant with cycles.

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