IMPACT CHARACTERIZATION OF POLYMER COMPOSITES BASED ON PEEK AND CARBON FIBRES

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Abstract
Considering the constant expansion of the areas of application of composite materials, is increasingly crucial to deepen the research for the correct evaluation of the potential application of these materials. In this job, the determination of the impact strength value, as well as the maximum load and the stiffness of the material, were obtained by means of an instrumented pendulum impact test. More in details, the characterization of four different composite materials, based on a polymeric matrix and reinforced with carbon fibres, will be presented. The materials tested differ for the type of reinforcement and the degree of crystallinity of their matrix. The influence of these factors on the aforementioned impact properties will be presented and discussed, leading to the identification of the composite material with the best impact properties for a specific application.

1. Introduction

1.1 Background and motivation

The opportunity of tuning the properties of an existing material in order to improve its characteristics, have increased the interest towards composites which are nowadays used in a broad range of applications such as engineering, industry, medical application [1, 2] and in all the fields where the demand of innovation and high performance is continuously increasing.

In this work, the impact properties of two carbon-fibre reinforced polyether-ether-ketone (CFR-PEEK) have been investigated by means of the instrumented pendulum impact test technique [3]. CFR-PEEK composites combine the excellent chemical characteristics of the PEEK matrix, which are kept at high temperature thanks to its high thermal resistance, with improved mechanical properties given by the carbon fibres used as reinforcement [4]. The materials will be judged according their response to the impact test in order to identify the most suitable method of preparation to enhance the impact properties.

1.2 Pendulum impact test

Fig. 1 illustrates the configuration of the pendulum impact test used in this work.

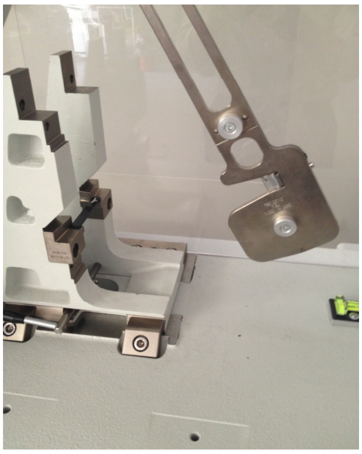

Figure 1. The Charpy impact setup. The instrumented impact hammer at the starting angle, the vice with shoulders and the specimen ready to be impacted are clearly identifiable in this photo of the experimental setup.

The specimen lies with its notched side centrally between two supports (shoulders) accordingly to *Charpy* configuration. This three-point bending configuration is commonly used to evaluate the toughness behavior of plastics under impact loading. In the notched Charpy impact test, a notch is cut into the specimen prior to impact. By notching, a stress concentration as well as in increase in crack propagation rate is achieved at the front of crack tip [5].

For the Charpy test, pendulum hammers accordingly ISO 13802 are commonly suggested, with nominal impact energies in the range of 0.5 to 50 Joule and impact velocities of 2.9 and 3.8 m/s, depending on the impact energy [6]. When the test is performed, the energy absorbed is calculated from the difference between the pendulum height before and after the impact. Furthermore, the meaningfulness of the notched Charpy impact test can be significantly increased by the electronic recording of force-displacement diagrams or force-time curve obtained by means of the instrumented notched Charpy impact test technique [7, 8].
From the acquired force versus time plot, taking into account the Newton's second law, it is possible to determine the impact velocity by integration and, also by integration, the displacement as a function of time (equation 1).

$$\varepsilon = \iint \frac{F(t)}{m_H} d^2t \qquad (1)$$

where m_H represents the mass of the pendulum hammer used.
Once the force and displacement/deflection (ε) are known for a defined instant of time t, it is possible to calculate the energy absorbed up to a specific deflection by determining the area under the force-deflection curve, that means by integrating in accordance with the formula given in equation 2:

$$E_{abs} = \int_0^{s_b} F(\varepsilon) \cdot d\varepsilon \qquad (2)$$

where E_{abs} represents the specimen absorbed energy and s_b is the deformation at break. The Charpy impact strength of a notched test specimen (R_{CN}) can be calculated dividing the energy thus obtained by the cross-section of the specimen, according to the formula given into equation 3:

$$R_{CN} = \frac{E_{abs}}{h \cdot b_N} \cdot 10^3 \qquad (3)$$

where h is the thickness of the specimen and b_N is the width remaining at the base of the notch. The Charpy impact strength is commonly expressed in kJ/m^2.

2. Experimental work

The applicability of the Charpy instrumented technique to composite has been proved by many different authors and papers [9]. The graph obtained by means of an instrumented test can be considered as the "fingerprint" of that material, giving the clear understanding of its behavior during an impact event and its possible employment for any specific application. For this reason, it has been identified as the simplest and reliable experimental method to characterize the CFR-PEEK under analysis.

2.1 Materials

The two kind of composites tested in this study are essentially the same in terms of components (CFR-PEEK) and ratio between matrix and reinforcement (30% wt carbon fibres). They only differ for the different nature and consequent structure of the carbon fibres used.

In one case the composite is made using PAN (PolyAcryloNitrile) carbon fibres, which are polymer derived. Their structure confers high anisotropy and in particular higher strength along the direction of the fibres. In the other case the reinforcement is made of PITCH carbon fibres. These fibres don't have a polymeric nature, but their precursors are low molecular weight aromatic hydrocarbons. The structure of PITCH carbon fibre reinforcement is random and gives less strength to the final composite compared to PAN carbon fibres, but on the other hand it also gives more isotropic properties.

In both cases the process used to prepare the samples is the injection molding technique. Since this process is done at high temperature and high pressure, the thermal history can affect final properties, such as the crystallinity, according to Avrami's equation (Eq. 4), and as a consequence the mechanical properties.

$$y = 1 - e^{-kt^n} \qquad (4)$$

k and n are cinematic constants un-dependent on time, which values depends on the crystallization system. While y is the crystallized fraction which is a function of time. For this reason, samples obtained at different cooling time, 40 and 55 seconds respectively, were tested for both CFR composites presented in this work.

To summarize, a total of four different samples had been prepared, by using two different matrixes, of the same polymer, coupled with two different carbon-fibre-reinforcement:
- Invibio® PEEK-OPTIMA® reinforced with PAN carbon fibres obtained at two cooling times: short (40 seconds) and long (55 seconds).
- Invibio® PEEK-MOTIS® reinforced with PITCH carbon fibres obtained at two cooling times: short (40 seconds) and long (55 seconds).
In both cases, and for both cooling times, specimens were bars shaped with dimensions 8.0 x 3.3 x 80 mm (Width x Thickness x Length).

2.2 Specimen preparation

The samples were supplied in form of bars with a width smaller than what is required by the international standard, but the resilience calculation is not affected since it doesn't take this dimension in account.

The bars were notched using an automatic Instron CEAST AN50 notching machine with the appropriate knife to make a V notch (45° angle, radii 0.25 and 1 mm). After this operation the samples were let one day aside and not immediately impacted, to avoid the residual stress after the notching procedure. The quality and the dimensions of the notches had been checked by means of a digital optical microscope Mitutoyo model AT112-120F. A typical example is shown in figure 2.

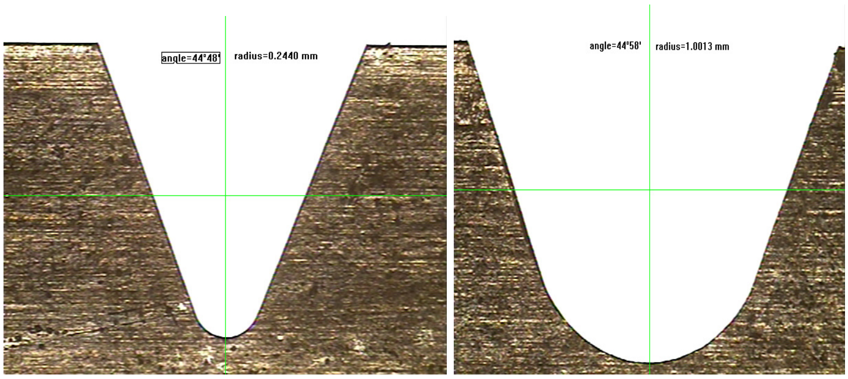

Figure 2. Typical example of 0.25 mm (left) and 1.00 mm (right) radius notch obtained in the CFR-PEEK specimens are shown.

2.3 Testing procedure

The impact tests were performed adopting the Charpy ISO 179-2 method as guideline. After some preliminary impacts, the brittle nature of these materials have been clearly seen. In order to obtain more consistent and reliable results, a notch according to type B (1 mm radius) [8] was selected as the most suitable for these CFR-PEEK composite materials. The largest radius allow to reduce at minimum the embrittlement but at the same time promotes the fracture initiation and propagation consequently to the impact [10].

In addition, the impact velocity had also shown a great effect on the dynamic of the curves acquired and for this reason tests were finally performed at 1 m/s, in agreement with both ISO 179- 2 and 17281 methods [11]. At speed of several meters per second the dynamic effects are not negligible, leading to oscillations in the recorded quantities. At velocities approaching 1 m/s the dynamic effect may become significant but still controllable, allowing a more precise evaluation of the impact resistance [12].

To do that, an Instron CEAST 9050 motorized pendulum has been used. The impact hammer selected had a potential impact energy of 7.5 J at 150°, the default release angle. Due to the fact that starting angle has been modified down to 30°, to achieve the impact velocity of 1 m/s, the potential impact energy has been consequently reduced down to 0.54 J.

The instrumented hammer used is equipped with a strain-gauge sensor and its range of acquisition was set equal to 1 kN. Load data have been collected by means of a dedicated acquisition system and software, having selected a sampling frequency of 2 MHz and an acquisition time of 2.5 ms.

3. Experimental results and discussion

3.1 Impact test of PAN CFR-PEEK OPTIMA

The force versus displacement traces obtained for this composite, for both cooling times, are very repeatable and essentially linear upon maximum load (peak force). The crack initiates immediately after this point, propagating very rapidly as shown in the sharp decrease of the measured force signal. Figure 3 is showing a typical force-displacement curve obtained by testing the material under analysis.

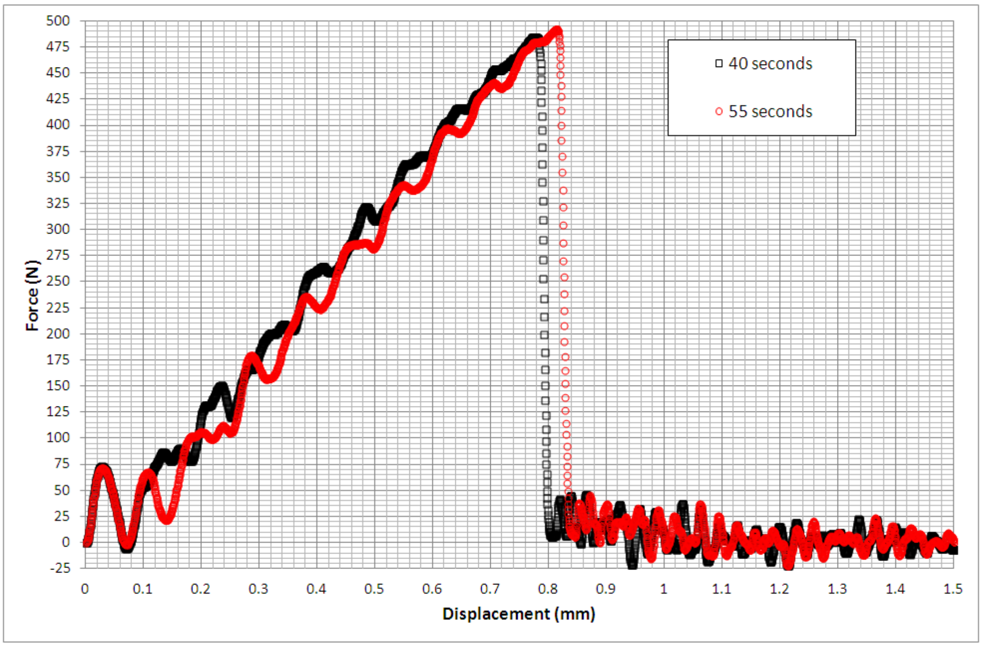

Figure 3. A typical Charpy impact test example showing force-deformation curves obtained with PAN reinforced PEEK-Optima at 1m/s with impact energy 0.54 Joule. The black squared curve refers to the material cooled for 40 seconds while the red circled one represents the material cooled for 55 seconds.

For each specimen impacted the peak force value, the maximum load bears during impact, as well as the impact strength, according to the equation 3, have been evaluated. Furthermore, due to the fact that test conditions are in quite good agreement with the requirements of ISO 17281 method [11] and plastic deformation is totally absent for both samples, the stiffness [13], defined as per equation 5, had been evaluated:

$$S = \left(\frac{dF}{d\varepsilon} \right)_{\varepsilon \to 0} \qquad (5)$$

This value can provide an estimation of the elastic modulus of the material, due to the fact that it is directly dependent on the stiffness. The proportionality factor is given by a constant value depending basically on the dimensions of the specimen.
To obtain the stiffness value, a computer-aided curve-fitting procedure had been used to draw a smooth mean force-deformation curve through the experimental record. A polynomial curve was selected as fitting equation considering the amount of data from beginning of the impact, excluding the inertial peak, until maximum force. The slope of the curve was evaluated directly from the fitting curve.

Same testing conditions, as well as same data analysis, were used to collect data for ten bars for each sample. The same test was also repeated in another day, in order to increase statistics collected. Mean value and standard deviation of the average value were calculated for all results.

Data obtained for the PAN CFR-PEEK with cooling of 40 seconds are reported into Table 1 while those for the same material cooled for 55 seconds are reported into Table 2.

PAN-PEEK 40s	**Thickness [mm]**	**Width [mm]**	**Peak Force [N]**	**Impact Strength [kJ/m^2]**	**Stiffness [N/mm]**
Mean	3.320	8.120	484	7.32	673
St.Dev. Mean	0.001	0.008	3	0.08	4

Table 1. The mean values and the standard deviation of the mean for the PEEK material reinforced with PAN carbon fibres and cooling time 40 seconds are reported.

PAN-PEEK 55s	**Thickness [mm]**	**Width [mm]**	**Peak Force [N]**	**Impact Strength [kJ/m^2]**	**Stiffness [N/mm]**
Mean	3.320	8.160	496	7.62	679
St. Dev. of Mean	0.002	0.002	2	0.06	4

Table 2. The mean values and the standard deviation of the mean for the PEEK material reinforced with PAN carbon fibres and cooling time 55 seconds are reported.

3.2 Impact test of PITCH CFR-PEEK MOTIS

In the following, the experimental results for the composite material PEEK-MOTIS reinforced with PITCH carbon fibres are discussed for, respectively, cooling time of 40 seconds (Table 3) and 55 seconds (Table 4).

The test conditions, as well as the data analysis, the number of specimens impacted and the number of test, are the same as discussed in the previous section. In Figure 4, an example of impact curves acquired testing this material is shown.

PITCH-PEEK 40s	Thickness [mm]	Width [mm]	Peak Force [N]	Impact Strength [kJ/m^2]	Stiffness [N/mm]
Avg	3.340	8.050	358	5.68	461
St. Dev. of Mean	0.001	0.002	3	0.06	2

Table 3. The mean values and the standard deviation of the mean for the PEEK material reinforced with PITCH carbon fibres and cooling time 40 seconds are reported.

PITCH-PEEK 55s	Thickness [mm]	Width [mm]	Peak Force [N]	Impact Strength [kJ/m^2]	Stiffness [N/mm]
Avg	3.330	8.200	370.5	5.93	464
St. Dev. of Mean	0.001	0.000	2	0.05	3

Table 4. The mean values and the standard deviation of the mean for the PEEK material reinforced with PITCH carbon fibres and cooling time 55 seconds are reported.

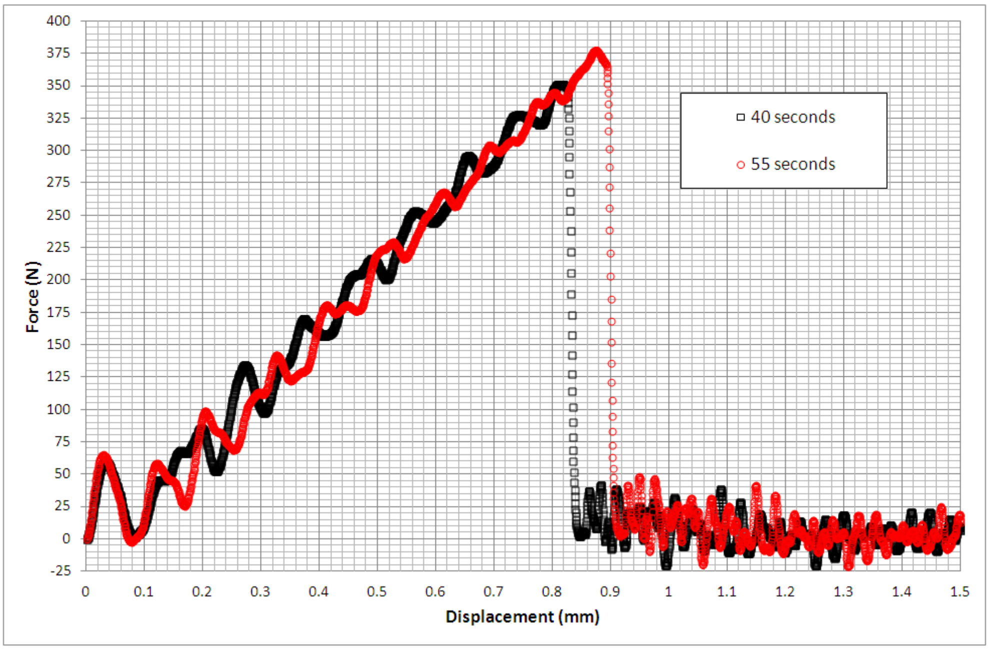

Figure 4. A typical Charpy impact test example of force-deformation curves obtained with PITCH reinforced PEEK-Motis at 1m/s with impact energy 0.54 Joule. The black squared curve refers to the material cooled for 40 seconds while the red circled one represents the material cooled for 55 seconds.

4. Conclusions

Comparing the results obtained testing the material CFR-PEEK-Optima can be clearly seen a slight, but not negligible, increment of all impact properties cooling the material for 55 seconds. This effect, driven by the extended cooling time, is due to the increase of the crystallinity into the polymer PEEK matrix, in agreement with the Avrami's law (equation 4). The ordered structure shows an improved resistance to impact because it is able to more evenly disperse the energy during the impact and fracture propagation [14]. The most significant growth has been obtained for the impact strength value, with a variation of about 4%.

An analogous comparison was done for the CFR/PEEK-Motis where, once again, a generic slight increase in the impact properties has been reported increasing the cooling time. For the stiffness and maximum force the gain is of the same order of magnitude of the previous material. Nevertheless, in this case the impact strength value is not growing as in the previous case, and the growth is of about 3%.

If materials are now compared between each other, it is clearly evident that the former (CFR-PEEK-Optima) has better impact properties in comparison to the latter (CFR-PEEK-Motis). The interpretation of the experimental results is also finding a support into literature, where is definitely well known that PAN fibres shown an higher resistance respect to PITCH ones.

For all these reasons, the material showing the best impact performance is the CFR-PEEK-Optima with a cooling time of 55 seconds. The instrumented Charpy impact technique allows to evaluate the impact properties which, in this case, are contributing to select the most suitable composite material for a particular biomedical application.

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