

IMPACT CHARACTERIZATION OF POLYMERS COMPOSITES BASED ON PEEK AND CARBON FIBRES

A. Calzolari^{a*}, M. Tommasone^a, M. Zanetti^b, M. Regis^b and F. D'Acerno^b

^aITW Test & Measurement Italy, Via Airauda 12 Pianezza (TO) ITALY

^bMaterial Science Department, University of Turin ITALY

*andrea.calzolari@instron.com

Keywords: Impact, Composite, PEEK, Characterization

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 rigidity of the material, has been 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 will differ for the type of the reinforcement and the degree of crystallinity of their matrix. The influence of these factors on the aforementioned impact properties will be the 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 fibers used as reinforcement [4]. The materials will be judged according their response to the 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.

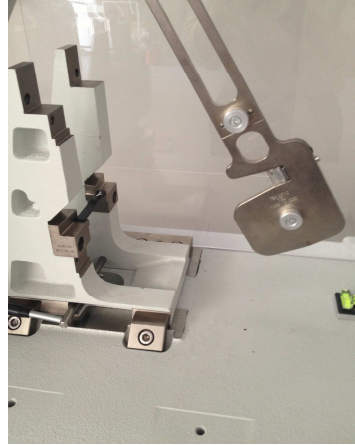


Figure 1. The Charpy impact setup where it can be clearly seen the impact hammer, the vice and the specimen ready to be impacted.

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 an 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 and 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).

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

where m_H represents the mass of the pendulum hammer used.

Once the force and displacement/deformation (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:

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

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 so obtained by the cross-section of the specimen, according to the formula given into equation 3:

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

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 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 some specific applications. 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 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 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, and 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 gives also more isotropic properties.

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

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

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 at different cooling time, 40 and 55 seconds respectively, have been tested for both kind of composites presented in this work.

To summarize, a total of four different samples have been prepared, by using two different matrixes coupled with two different carbon-fibre-reinforcement:

- Invibio[®] PEEK-OPTIMA[®], a PEEK composite reinforced with polyacrylonitrile (PAN) carbon fibers (30% wt). Bars with dimensions 8.0 x 3.3 x 80 mm (Width x Thickness x

Length) were prepared by injection moulding at two different cooling time: short (40 seconds) and long (55 seconds) cooling time.

- Invibio[®] PEEK-MOTIS[®], a PEEK composite reinforced with PITCH carbon fibers (30% wt). Bars with dimensions 8.0 x 3.3 x 80 mm (Width x Thickness x Length) were prepared by injection moulding at two different cooling time: short (40 seconds) and long (55 seconds) cooling time.

2.2 Specimen preparation

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

The bars have been notched using an automatic Instron CEAST AN50 notching machine with the appropriate knife to make a V notch (45° angle, radius 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 have been checked by means of a digital optical microscope Mitutoyo model AT112-120F. A typical example is shown in figure 2.

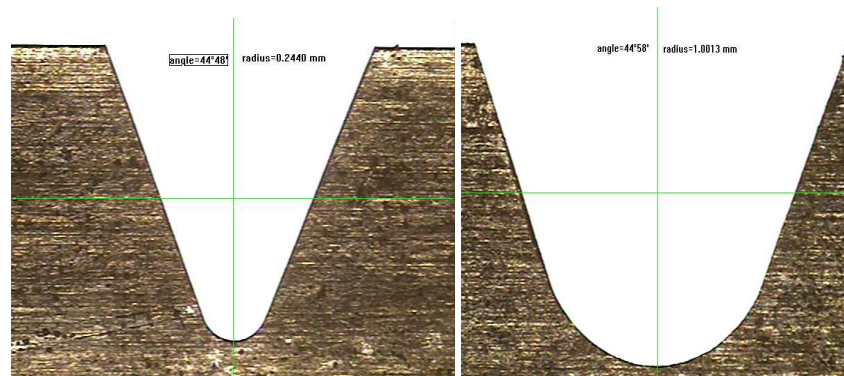


Figure 2. Typical example of 0.25 mm (left) and 1.00 mm (right) radius notch obtained in the CFR-PEEK specimens have been shown.

2.3 Testing procedure

The tests have been performed by adopting the Charpy ISO 179-2 method but with a derogation from some parameters. This was due to the fact that 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] have been selected as the most appropriate for these CFR-PEEK composite materials. The notch is a stress-concentration area which promotes a brittle rather than ductile failure on the specimen. 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 has also shown a great effect on the quality of the curves acquired and for this reason tests have been done at 1 m/s, in agreement with ISO 17281 method [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, a CEAST 9050 motorized pendulum equipped with Charpy accessories according to the aforementioned standards have been used. The impact hammer selected had a potential impact energy of 7.5 J at 150°, the default release angle. But, due to the fact that starting angle has been modified down to 30° in order to achieve the impact velocity of 1 m/s, the potential impact energy has been 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

The current section present the experimental results obtained. The CFR-PEEK material reinforced with PAN carbon fibres will be discussed first, followed by the CFR-PEEK reinforced with PITCH fibres.

3.1 Impact test of PAN CFR-PEEK OPTIMA

The force versus displacement trace obtained for this, as well as for the second material presented later on, is 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.

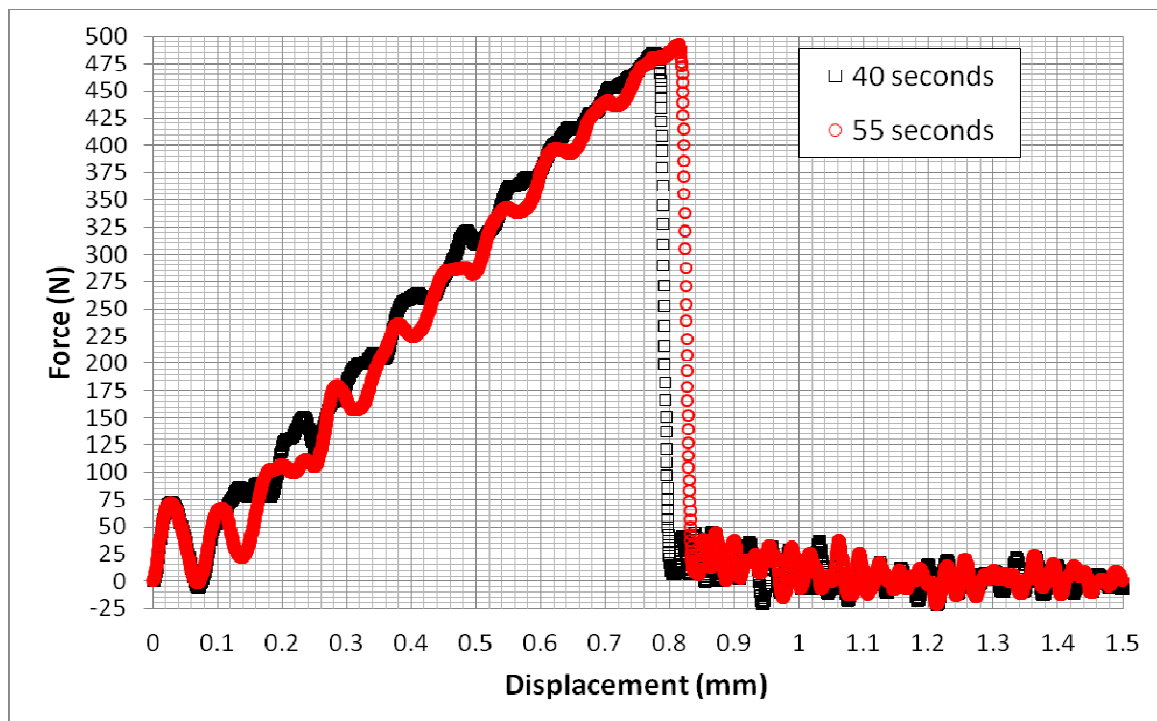


Figure 3. A typical example of force-deformation curves for the Charpy impact test with PAN reinforced PEEK-Optima at 1m/s with impact energy 0.54 Joule. The black squared curve is referring to the material cooled for 40 seconds while the red circled one is referring to the material cooled for 55 seconds.

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] we also tried to evaluate the stiffness of the material [13], defined as per equation 5:

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

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 essentially on the dimensions of the specimen.

In order to obtain the stiffness value, a computer-aided curve-fitting procedure has been used to draw a smooth mean force-deformation curve through the experimental record. A polynomial curve has been used 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 has been evaluated considering the central section of the fitting curve where the linearity can be guaranteed with a 5% of tolerance.

This testing process, as well as the aforementioned data analysis, has been repeated for ten bars of the same material. Furthermore, in order to have two complete set of experimental data, the test has been repeated by using the same test conditions in another day. With the data collected, mean value and standard deviation of the average value have been calculated.

The final results 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	483.7	7.325	673.5
St.Dev. Mean	0.001	0.008	3	0.077	4

Table 1. The mean value, as well as the standard deviation of the mean, are shown for the material PEEK reinforced with PAN carbon fibres and cooling time 40 seconds.

PAN-PEEK 55s	Thickness [mm]	Width [mm]	Peak Force [N]	Impact Strength [kJ/m ²]	Stiffness [N/mm]
Mean	3.320	8.160	496.4	7.6155	678.9
St. Dev. of Mean	0.002	0.002	2	0.0625	4

Table 2. The mean value, as well as the standard deviation and the standard deviation of the mean, are shown for the material PEEK reinforced with PAN carbon fibres and cooling time 55 seconds.

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 shown for, respectively, cooling time of 40 seconds (Table 3) and 55 seconds (Table 4).

The test conditions, as well as the method used to analyze the data, the number of specimens impacted and the test number, are the same as discussed for previous material reinforced with PAN carbon fibres. In Figure 4 an example of impact curves acquired testing the material under analysis.

PITCH-PEEK 40s	Thickness [mm]	Width [mm]	Peak Force [N]	Impact Strength [kJ/m ²]	Stiffness [N/mm]
Avg	3.340	8.050	358.3	5.684	461.3
St. Dev. of Mean	0.001	0.002	3	0.065	2

Table 3. The mean value, as well as the standard deviation of the mean, are shown for the material PEEK reinforced with PITCH carbon fibres and cooling time 40 seconds.

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	5.933	464.1
St. Dev. of Mean	0.001	0.000	2	0.052	3

Table 4. The mean value, as well as the standard deviation of the mean, are shown for the material PEEK reinforced with PITCH carbon fibres and cooling time 55 seconds.

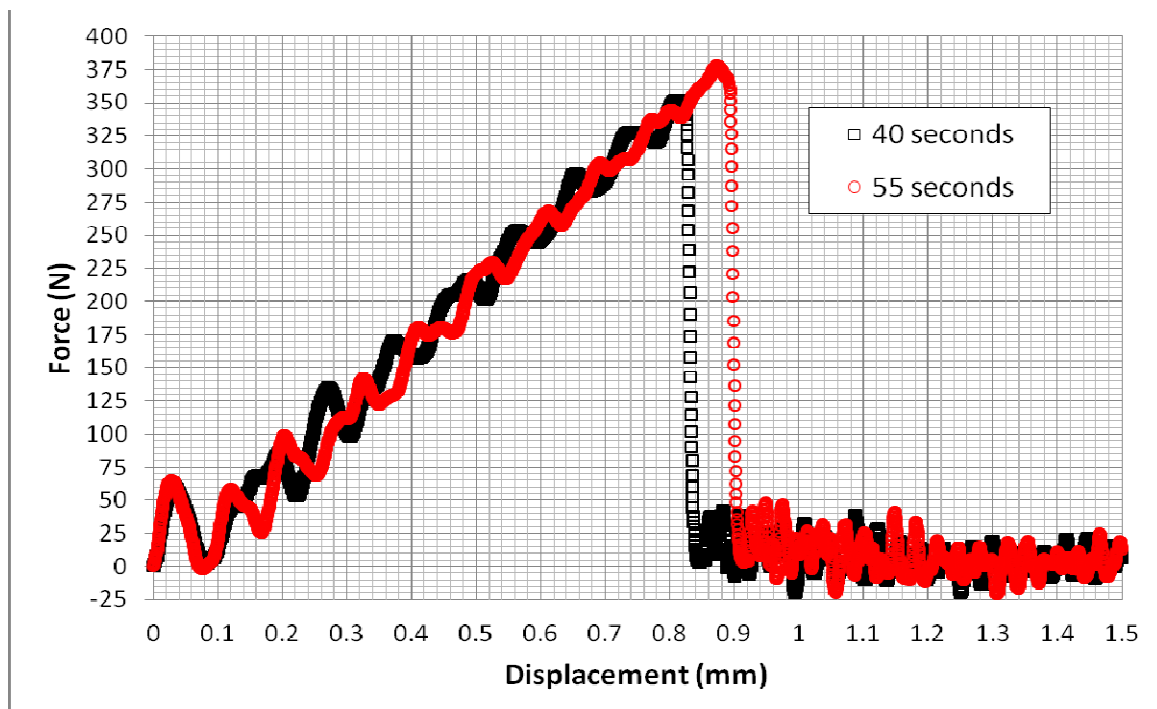


Figure 4. A typical example of force-deformation curves for the Charpy impact test with PAN reinforced PEEK-Optima at 1m/s with impact energy 0.54 Joule. The black squared curve is referring to the material cooled for 40 seconds while the red circled one is referring to the material cooled for 55 seconds.

4. Conclusions

Comparing the results (reported into Tables 1 and 2) obtained testing the material CFR-PEEK-Optima it can be clearly seen a slight generic increase of all impact properties cooling the material for 55 seconds. This effect, driven by the increased cooling time, is generated by the increase of the cristallinity of the PEEK matrix, in agreement with the Avrami's law (equation 4).

The ordered structure shows an higher resistance to impact because it is able to more evenly disperse the energy during the impact and fracture propagation [14]. The increase of the stiffness is quantified into 0.8% while the peak force is growing of about 2.5% increasing the cooling time. Nevertheless, the most relevant increment has been obtained into the Impact Strength value, with a variation of about 3.8%.

An analogous comparison was done for the CFR/PEEK-Motis where, as obtained for the previous material, a generic slight increase if the impact properties has been reported increasing the cooling time, with a correspondent increase of the cristallinity ratio of the structure. The stiffness increase is more or less of the same order of magnitude, 0.5%, while the peak force is about 2.7% higher. With this material the Impact Strength value is not growing as in the previous case, but is increasing of about 2.8%.

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). With the Optima the stiffness is higher than 46% respect to Motis, the Peak force is higher than 34% while the Impact Strength value of about 28%. The interpretation of the experimental results is also finding a support into the 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. This characterization, obtained considering the impact properties, will contribute to select the most appropriate material for a particular biomedical application.

References

- [1] S. M. Kurtz and J. N. Devine. PEEK biomaterials in trauma, orthopedic, and spinal implants. *Biomaterials*, 28(32): 4845–4869, 2007.
- [2] S. C. Scholes and A. Unsworth. Pitch-based carbon-fibre-reinforced poly (ether-ether-ketone) OPTIMA® assessed as a bearing material in a mobile bearing unicondylar knee joint. *Journal of Engineering in Medicine*, 223(1): 13–25, 2009.
- [3] W. Grellmann. Charpy Impact Test and Charpy Notched Impact Test, In *Polymer Testing*, 150-155. Hanser, Munich, 2007.
- [4] H. F. Mark and J. I. Kroschwitz. *Encyclopedia of polymer science and engineering*. Wiley, 1985.
- [5] M. Takano and L. E. Nielsen. The notch sensitivity of polymeric materials. *Journal of Applied Polymer Science*, 20(8): 2193–2207, 1976.
- [6] ISO 13802. *Plastics – Verification of pendulum impact machines – Charpy, Izod and tensile impact-testing*, 1999.
- [7] R. A. Wullaert. Applications of the Instrumented Charpy Impact Test. *Impact Testing of Metals, ASTM STP 466*. American Society for Testing Materials, 148-164, 1970.

- [8] ISO 179-2. *Plastics – Determination of Charpy impact properties – Part 2: Instrumented impact test*, 1997.
- [9] M. R. Kessler. Instrumented Charpy Impact Machines, In *Advanced Topics in Characterization of Composites*, 101-102. Trafford Publishing, Victoria, 2004.
- [10] A.T. Gavelis, M.J. Wioncek and R. Malloy. The effect of notching method and notch radius on the impact performance of injection molded thermoplastics. *The Journal of Injection Molding Technology*, 2(1): 18-22, 1998.
- [11] ISO 17281. *Plastics — Determination of fracture toughness (GIC and KIC) at moderately high loading rates (1 m/s)*, 2002.
- [12] A. Pavan.ESIS TC4 Activity on High Rate Testing of Plastics. *Proc. 12th European Conference on Fracture – ECF12*, 3(1): 363-368, 1998.
- [13] ISO 13586. *Plastics — Determination of fracture toughness (GIC and KIC) — Linear elastic fracture mechanics (LEFM) approach*, 2000.
- [14] J. P. Mercier, J. J. Aklonis, M. Litt and A. V. Tobolsky. Viscoelastic behavior of the polycarbonate of bisphenol. *Journal of Applied Polymer Science*, 9(2), 447–459, 1965.