Bulk mechanical properties of thermoplastic poly-ε-caprolactone.

K. Ragaert, L. Cardon
CPMT, Department of Industrial Technology and Construction, Faculty of Engineering and Architecture, Ghent University, Belgium

I. De Baere, J. Degrieck
Department of Materials Science and Engineering, Faculty of Engineering and Architecture, Ghent University, Belgium

ABSTRACT: Poly-e-caprolactone (PCL) is a very popular material for the 3D plotting of scaffolds for tissue engineering. It is investigated in applications for bone as well as cardiovascular tissues. Porous PCL scaffolds have been widely characterized in terms of mostly compression and bending properties, but knowledge on the bulk mechanical properties of the PCL polymer itself is lacking, while these are the properties that would be needed for correct finite element modelling (FEM) of the scaffold's behaviour under mechanical loading. Within the current research, the bulk mechanical properties of PCL were investigated on injection moulded parts in tension, compression and flexure. These properties are reported here, so they may be used in further research which included FEM of PCL-based scaffolds.

1 INTRODUCTION

Poly-ε-caprolactone (PCL) is a thermoplastic semi-crystalline aliphatic polyester. It can be obtained through ring-opening polymerization of ε-caprolactone. The reaction takes place under the influence of catalysts and added heat. The polymer contains an ester linkage which is hydrolytically unstable (Wright 2004; Nair and Laurencin 2007), allowing for a breakdown into caproic acid, which is well-tolerated by the human body (Perale, Pertici et al. 2008). PCL is widely used in research as a base material for scaffolds because it

(i) is relatively flexible in comparison to PLA and PGA and as such is considered more suitable for use with scaffolds for cardiovascular application (Brody and Pandit 2007);

(ii) displays very good thermal stability. Its degradation temperature is situated in the range of 280 to 330°C (Sivalingam and Madras 2003), which makes it very suitable for use with a melt processing technique like the micro-extrusion for 3D plotting proposed within this work;

(iii) is FDA-approved; it is considered to be compatible with both hard and soft tissues and will degrade slowly in the human body over a period of 24 to 36 months (Nair and Laurencin 2007; Lam, Hutmacher et al. 2009);

(iv) is relatively cheap.

While much is reported on the mechanical properties of porous PCL scaffolds, literature is rather scarce on the bulk mechanical properties of PCL itself. Some tensile properties may be retrieved from literature (Lepoittevin, Devalckenaere et al. 2002; Rosa, Neto et al. 2004), but no information can be found on the true bulk properties in flexure or compression, a fact which has been noted also by Das and coworkers (Eshraghi and Das 2010). The lack of published data on the compressive properties of PCL seems odd, since much research is done on the compressive strength of PCL scaffolds which are used for bone tissue replacement (Shor, Guceri et al. 2007; Estelles, Vidaurre et al. 2008; Guarino, Causa et al. 2008; Cahill, Lohfeld et al. 2009; Lam, Hutmacher et al. 2009; Shor, Guceri et al. 2009; Eshraghi and Das 2010).

Some researchers investigating scaffolds have considered non-porous parts made with their scaffold production technique to be representative of the bulk mechanical properties. Cahill et al. reported a tensile modulus of 47 ± 5 MPa for sintered dogbones (Cahill, Lohfeld et al. 2009), while Shor et al. reported a compressive modulus of 109 ± 2.3 MPa for a non-porous 3D-plotted part (Shor, Guceri et al. 2009). However, these values are so far removed from one another as well as the tensile modulus reported by the manufacturer (Perstorp 2003), that the need arises to investigate the properties of actual bulk PCL parts.

Within this work, the bulk mechanical properties of a PCL material commonly used for scaffold production are determined. These properties may be used to compare the polymer to other scaffold materials used for tissue engineering and – in future work – to create finite element models of the scaffolds so as to predict their behaviour under loading conditions.

2 MATERIALS AND METHODS

2.1 *Materials*

The PCL material used is PCL CAPA 6500 from Perstorp (UK). The manufacturer reports a weight-averaged molecular weight (M_w) of 84500 Da, a polydispersity of 1.78 and a maximum crystalline fraction of 56%.

2.2 *PCL bulk test specimens*

The specimens for the evaluation of the mechanical properties were injection moulded on a 800 kN injection machine (Engel, Austria) with a 30 mm injection screw. Three different parts were manufactured in a single multi-cavity mould. The different specimens include a dog-bone geometry for tensile testing (gauge length 36 mm, gauge width 6.35 mm and thickness 4mm), a rectangular bar (120*13*3 mm^3) for flexural testing and a square plate (50*50*4 mm^3) for compression testing.

It is noted that (i) the dimensions of the moulded parts will be slightly smaller due to shrinkage of the polymer upon cooling and (ii) these dimensions do not match exactly those specified in the relevant standards listed further on. For the determination of the mechanical properties, all calculations were based on the measured actual dimensions of the specimens.

Fifty injection runs were performed, from which parts were then selected as test specimens based on a visual inspection of their dimensions and moulding quality.

2.3 *Bulk mechanical properties*

All experiments were performed on a tensile testing apparatus INSTRON 5800R (Instron, Belgium) and the data acquisition was realized with LABVIEW software (National Instruments, Belgium). For all experiments, three specimens were tested and their results were averaged. The standards followed for tensile, flexural and compressive testing were ASTM D412, D790 and D695 respectively. All values are averaged from at least three samples and are reported as mean ± standard deviation.

For the determination of ultimate tensile strength $\sigma_{max,t}$, strain at break $\varepsilon_{max,t}$ and yield strength $\sigma_{y,t}$, a load cell of 1 kN was used. The dog-bone specimens were loaded in tensile strain at a rate of 100 mm/min until failure. The large strains observed for PCL prevented the use of extensometers; maximum strain was hence derived from the crosshead's movement on the machine frame. Although strain values derived in this manner are not entirely accurate due to the deformation of the tensile tester itself, these deformations are considered negligible compared to the large strain values obtained by the PCL material. Any possible slipping of the specimen within the clamping claws was likewise considered negligible. For the determination of the tensile modulus E_t, the same load cell of 1 kN was used. An extensometer (INSTRON 2620-603, INSTRON, Belgium) was used to measure the strain ε_{xx}. The extensometer was used with a range of 1 mm travel over 10 mm, resulting in a maximum measured strain of 10% and E_t was determined as the slope of the linear part of the stress-strain curve, in the range of zero to 1% strain.

For the determination of flexural modulus E_{flex}, the same a load cell of 1 kN was used. The specimens were mounted in a 3-point bending setup, resting on two rounded supports (r = 1mm) with a support span length of 48 mm between them. In accordance with the standard, the test samples were indented with a rounded (r = 5mm) bar up to a maximum deflection of 6.4 mm, at a rate of 2 mm/min and E_{flex} was calculated as:

$$E_{flex} = \frac{L^3 \cdot m_f}{4 \cdot b \cdot d^3} \ [MPa] \qquad (1)$$

with:

- L the support span length [mm];
- m_f the slope of the load/deflection curve between the limits of 0 and 20N [N/mm];
- b the beam width [mm];
- d the beam thickness [mm].

For the determination of the compressive modulus, a load cell of 100 kN was used. Given the limited thickness of the samples, a relatively slow compression speed of 0.5 mm/min was used, to a maximum compression length of 0.25 mm. The compressive plates were treated with a lubricant in order to reduce friction and to improve the uni-axial compression state. No linear variable differential transformers (LVDTs) could be used to measure strain due to restricted space between the compression plates; therefore strain was deduced from the machine's movement. The compressive modulus E_{comp} was determined as the slope of the linear part in the stress-strain curve, which was situated between the stress levels of 10 and 15 MPa (~compressive force range of 25 to 37.5 kN). The strain levels in the compression test are much lower than during the determination of the absolute tensile properties and load levels are much higher, with a maximum compressive force of about 85 kN. As such, the deformation of the machine frame itself can no longer be considered negligible. To eliminate this deviation, a compensation factor $1/k_{frame}$ was determined by allowing the compressive plates to close onto one another at a rate of 0.5 mm/min and until a force limit of 85 kN. The value for $1/k_{frame}$ is the mean value (n = 3) of the linear slope of the load-displacement curve (F = 25 to 37.5 kN) for these experiments.

The modified displacement Δx_{mod} of the machine is then calculated as:

$$\Delta x_{mod} = \Delta x - {}^{1}/_{k_{frame}} \cdot F \quad [mm] \qquad (2)$$

with:

- Δx = the measured displacement value [mm];
- $1/k_{frame}$ = the compensation factor for the machine frame [mm/N];
- F = the measured force value [N].

The value of Δx_{mod} is used for the calculation of the compressive strain for the PCL part and finally, this strain value is used for the calculation of E_{comp} as described above. These last calculations are done via Matlab 7.10 software (Mathworks, The Netherlands), where a 5-step progressive filter is also added to the compression curve to filter out the noise.

3 RESULTS AND DISCUSSION

3.1 *PCL tensile properties*

During the tensile testing of the PCL parts, it is remarkable how much the material deforms plastically before actually breaking. Figure 1 shows different moments during the tensile test: once necking of the loaded region is initiated, it will continue to propagate along the entire length of the dog-bone bar, leading to very high strain values.

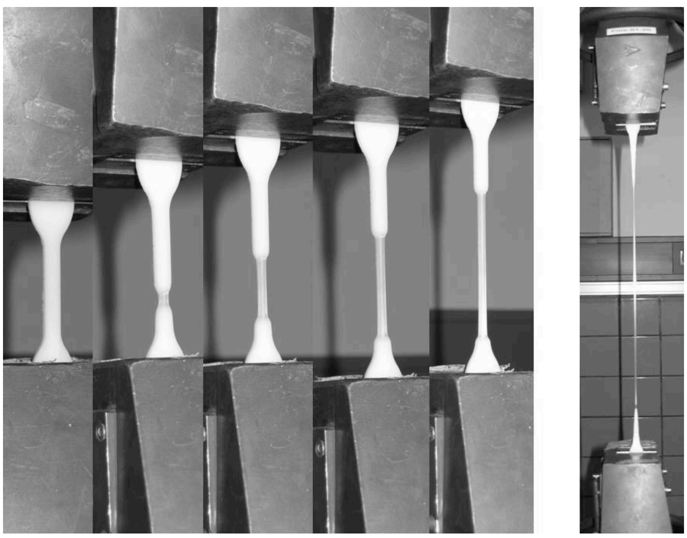
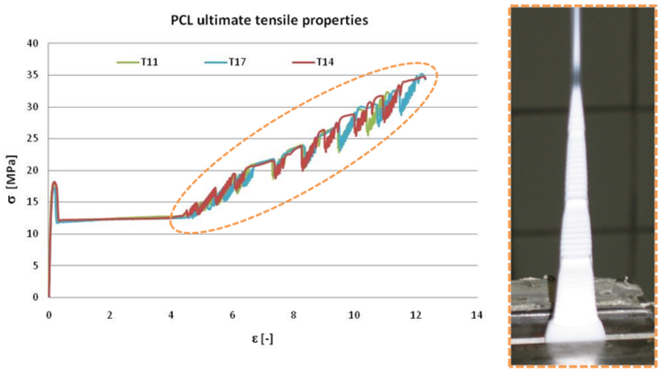


Figure 1: Tensile testing of PCL.

In Figure 2(a), the results of the tensile tests to failure are shown to be very reproducible, with the three curves overlapping one another closely even in the toothsaw-like profile towards the end of the curve. Once the yield strength is obtained around 17 MPa and necking of the polymer sets in, a sharp drop in engineering stress is observed, to a lower value of around 12 MPa. From there, stress hardly rises for a large straining interval (up to an elongation of 150 mm, which corresponds to roughly 400% strain), indicating that the plastic material deformation propagates very easily once initiated. These large deformations are possible because PCL is in the leathery state at ambient temperatures, as was demonstrated by the DSC experiment. It can also be observed that the plastically deformed region becomes more transparent, an indication that the crystalline regions of the polymer are being destroyed (Osswald and Menges 2003), which happens by internal slipping of polymer chains after they have been aligned to their fullest possible extent (Sperling 2006; Callister and Rethwisch 2010).

The final ascent of the stress-strain curve displays significant fluctuations before break finally occurs at large deformation levels. Once the entire length of the dog-bone bar has been plastically deformed by necking, it is observed that even the broader handles of the dog-bone are deformed, by a tiered slipping of



(a) (b)

Figure 2: (a) Ultimate tensile properties of PCL and (b) tiered deformation of dog-bone handle.

material sections, as can be seen in Figure 2(b). This causes the toothsaw-like profile of the failure region.

A similar shape was obtained for the stress-strain curve of pure PCL (Union Chemical Carbide, M_w = 80,000 Da) by Rosa et al. (Rosa, Neto et al. 2004), albeit with different strain levels (which is attributed to the differently shaped test specimens they used): a sharp rise to a yield strength of 16.9 MPa (at strain levels of 25%), followed by a drop in engineering stress to a plateau of about 13 MPa which is maintained until a strain of 100% before the curve rises towards the break point. They did not report the deformation mechanism which takes place in the dog-bone handles.

The mean tensile strength of PCL is calculated as $\sigma_{max,t}$ = 34.1 ± 1.5 MPa; strain at the onset of the tiered deformation is 438 ± 6% and the strain value at ultimate failure supposedly is over 1000%, but this value is calculated in reference to the start

length that did not include the dog-bone handles and therefore not considered representative. The yield strength was determined as $\sigma_{y,t}$ = 17.82 ± 0.47 MPa. Given the large plastic deformations, it would be advisable to consider the yield strength as a top limit for the practical use of PCL parts instead of the ultimate tensile strength. Finally, the tensile modulus is derived as E_t = 440 ± 15 MPa from the linear stress-strain regions.
Concerning the tensile properties acquired during these experiments, the ultimate properties $\sigma_{max,t}$ and $\varepsilon_{max,t}$ are slightly higher than those reported by Perstorp. Possibly, the tiered sliding deformation of the dog-bone handles did not occur in their tests, or they chose to disregard it and noted down the values obtained prior to the phenomenon. The value found for yield strength agrees very well with those values found in the data sheet and in literature; likewise, the tensile modulus correlates well with the value found by the manufacturer and by Rosa. Remarkably, Lepoittevin noted a much lower value. There is no immediate explanation for this. For the maximum strain $\varepsilon_{max,t}$, the strain level prior to the onset of the tiered deformation in the dog-bone handles is used, which is more representative as a limiting value for operational use of the polymer.

3.2 *PCL flexural properties*

The load-deflection curves for the bending experiments are shown in Figure 3. Especially during the linear ascent of the curve, the three tested samples appear to display similar behaviour.

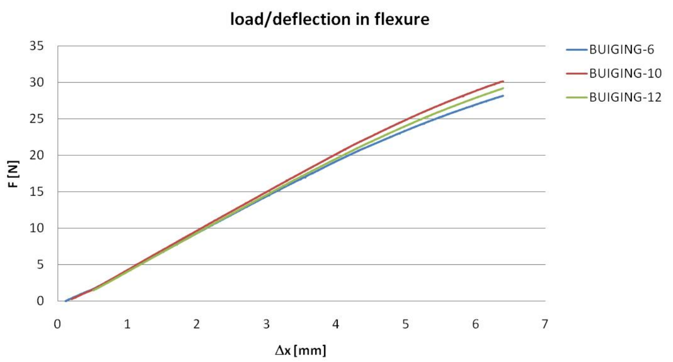


Figure 3: Load-deflection curves for the flexural testing.

The slope m_f of the curves is determined in the linear area of 2 to 10 N force; values for m_f range between 5.163 and 5.403 N/mm. The mean flexural modulus is calculated by Equation (1) as E_{flex} = 414 ± 10 MPa, which is somewhat lower than the value found for the tensile modulus. This is attributed to the fact that the load is applied transversal to the main polymer chain orientation.

3.3 *PCL compressive properties*

Figure 4 shows the stress-strain curves for compression without considering the compensation for the straining of the machine frame.

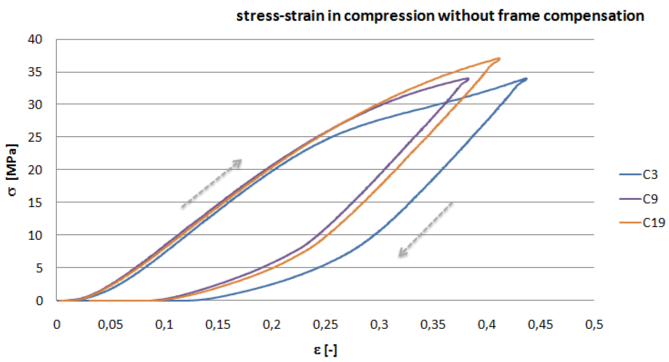


Figure 4: Stress-strain curves for compression (no compensation for frame).

The stress limits of 10 to 15 MPa were selected for the linear region in which E_{comp} will be calculated; this equals a force interval of 25 to 37.5 kN. The compensation curves (not shown) for the movement of the frame are highly reproducible and overlap one another. The compensation factor is determined as $1/k_{frame} = 9.0385*10^{-6} \pm 1.44*10^{-8}$ mm/N. This value is used for the recalculation of the compression curves between 10 and 15 MPa. The resulting curves are shown in Figure 5.

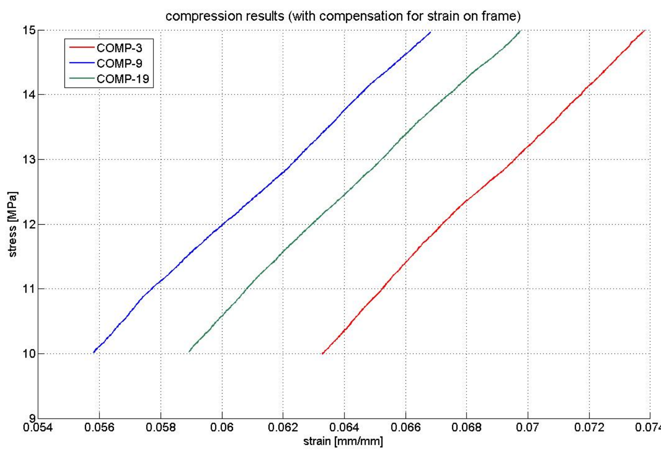


Figure 5: The stress-strain curves for compression, with compensation for frame.

Finally, the compressive modulus is calculated as E_{comp} = 455 ± 11 MPa, which relates well to the mean tensile modulus value of 440 MPa, especially considering that the friction between the plates and the test specimen will result in an apparently stiffer behaviour.

4 CONCLUSIONS

The mechanical properties were determined for tension, bending and compression. It was found that the tensile modulus $E_t = 440 \pm 3$ MPa, which relates well to the compressive modulus $E_{comp} = 455 \pm 2$ MPa. The flexural modulus was somewhat lower, with a mean value of $E_{flex} = 414 \pm 10$ MPa. The tensile yield strength amounted to 17.82 ± 0.47 MPa at a strain value of over 400%; once it was surpassed, necking of the polymer was expressed by a drop in the engineering stress and a large plastic deformation was observed without significant increase in stress levels. Finally, even the broader handles of the tensile dog-bone specimen were plastically deformed in a tiered manner.

The obtained material property values are very reproducible. They may be used in future to either compare candidate scaffold materials, or to model the mechanical behaviour of scaffolds under loading conditions.

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