MECHANICAL PROPERTIES OF TOUGH PLASMA TREATED FLAX FIBRE THERMOPLASTIC COMPOSITES

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Abstract
Natural fibres (NF) have shown to be a suitable alternative to glass fibres as reinforcing material in polymer composites since they offer similar specific strength and stiffness. Thus, those composites may be readily used in the automotive, sport and leisure. However, most of today's natural fibre applications are based on discontinuous fibre architectures, underrunning the performance of continuous synthetic fibre composites. Flax fibres show a great potential to be used as continuous reinforcing fibres in thermoplastic matrix composites. The use of high performance engineering polymers and the application of preceding plasma-based fibre surface treatments may further enhance the mechanical properties, making flax fibre thermoplastic composites an environmentally friendly alternative.
We investigated the mechanical behaviour of pure flax fibres, introduced an engineering polymer as matrix system, compared this material to commonly used matrices such as epoxy or polypropylene and studied the effect of two different plasma treatments on the mechanical performance of natural fibre composites (NFC). The influence of the plasma methods was found through composite failure testing. Results have shown, that composites with plasma treated fibres and engineering polymers along with a high fibre volume content offer a great potential as environmentally sustainable substitutes for synthetic composites in many applications.

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1. Introduction

Composites are increasingly used in mobility applications as for example in aerospace or in automotive for weight reduction and therefore energy consumption saving. The composites are usually carbon or glass fibres combined with a thermoset epoxy resin matrix. While the challenges for serial production of these materials are mostly solved, there are two major drawbacks of these materials: the high energy needed for the manufacturing of the fibres and the recycling of the thermoset composites at their end of life. These drawbacks could be addressed by using natural fibres in combination with thermoplastic matrix materials. Advantages such as high fracture toughness, high specific stiffness along with the natural fibres' carbon neutrality and the recyclability may be exploited. By the use of natural fibres, the energy consumption during the fibre manufacturing may be drastically reduced. Especially flax fibres, with its strong historical textile background, are a cost-effective and sustainable alternative to glass fibre composites. Amongst available natural fibres, flax exhibits a very high crystalline cellulose content (up

to 70 %) which is furthermore highly aligned (10 ° with the fibre axis), lending the fibre its excellent strength [1]. The hierarchical nature of the flax fibres, in addition, brings unique properties such as high damping. These natural fibre composites (NFC) have the potential to replace established materials in some applications, but many challenges in the fibre manufacturing and the composite processing must still be solved.
Matrices in natural fibre composites are usually thermosets (e.g epoxy (EP), vinyl ester, unsaturated polyester resins etc.) or thermoplastics (polypropylene (PP), polyethylene and polyvinylchloride etc.) [1, 2], whereas thermosets still outperform their thermoplastic counterparts in terms of mechanical properties, durability and the ability to be processed at room temperature. However, biodegradable polymers such as polylactic acid (PLA) and polyhydroxybutyrate (PHB) are increasingly gaining interest and consideration in NFC research, because of their ability to transform the composite into a fully biodegradable material. However, biodegradability often hinders high durability. Therefore, focus in this paper was on a high performance thermoplastic material, polyoxymethylene-copolymer (coPOM), with good mechanical properties along with good recycling potential.
In this paper, the mechanical testing results of flax fibres and considered matrix materials along with its composites properties are presented. The mechanical properties of coPOM were compared with those of EP, PP and poly-L-lactide acid (PLLA).

2. Specimen manufacturing

2.1. Materials

Single flax fibres and UD-woven flax fibre fabrics (ampliTex UD type 5009 (abbr. ampUD)) with an area weight of 300 g/m² were provided by Bcomp® Ltd. (Fribourg, Switzerland). Thermoplastic polymers were considered as matrix materials which should meet requirements such as inherently high tensile modulus and strength along with a heat deflection temperature above 100 °C and a melt temperature below 190 °C. Therefore, suitable materials have been identified, being poly lactide-L-acid (PLLA) and polyoxymethylene-copolymer (coPOM). The reference materials in this project were polypropylene (PP) (Sabic PP515A) and epoxy resin (Huntsman Araldite® LY 5052 / Aradur® 5052).

2.2. Fibre treatment

Several fibre surface treatments for natural fibres have been proposed in literature with the aim to overcome the inherent incompatibility between the fibre and thermoplastics. In general, those can be classified in underlying principles, being either chemically or physically. Chemical methods are usually characterised by the immersion of the fibre material into a dissolution [3], whereas with physical methods, the material is exposed to an electrically conductive atmosphere such as a plasma. Within this study, two physical treatments have been performed by Empa (St. Gallen, Switzerland), being a low pressure (LP) and an atmospheric pressure (AP) plasma treatment, based on plasma etching in Ar/CO_2 and in air, respectively. The main difference of these two technologies lies in the probability of collisions with present particles in the plasma. Within a low pressure environment, little collisions are likely to occur, thus electrons can activate the fibre surface directly and with a high energy. Conversely, due to collisions in AP plasma, electrons form metastables which have a remarkably lower energy and thus a lower fibre surface treatment impact, yet a higher incident particle flux. Both treatments have been performed using pilot plant reactors enabling reel-to-reel processing [4].

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2.3. Processing and composite preparation

The pure thermoplastic specimens were produced via injection moulding, whereas the pure epoxy specimens have been extracted out of a cast plate by water jet cutting.
For composite manufacturing, thermoplastic polymers have been brought into the shape of films. Therefore, films with a width of 80 mm and a thickness of approximately 100 μm were produced using a Collin® (Dr. Collin GmbH, Germany) Teach-Line extruder associated with a slit die.
The composites were manufactured via film stacking [5] using pre-dried fabrics (vacuum oven at 110–120 °C at 200 mbar for 15 minutes) and polymer films which have been stacked alternately in a steel mould. The target fibre volume content of 50 wt% was used in order to calculate the number of alternating layers required for flax fabric and polymer films. Six unidirectional (UD) flax layers were stacked to press coupons of about 2 mm thickness. The mould has been placed in a press and was heated up to 180 °C using a high pressure water heating system. Once that temperature was reached, a force of 96 kN was applied resulting in a cavity pressure of 10 bar. After 8 minutes pressing, the mould was cooled down whilst the pressure was maintained.
UD epoxy composites were manufactured via vacuum-assisted resin infusion (VARI).

3. Experiments

3.1. Fibre characterisation

The ampliTex UD flax fibres obtained from Bcomp® have been analysed with respect to their mechanical and thermal properties. Tensile tests according to ASTM D3822-08 were performed on single fibres, which refers to the so-called elementary fibre within the flax stem. The tests were carried out using a universal yarn testing machine having 1 N load cell. The tests were carried out with a specimens' gauge length of 40 mm and a displacement controlled loading rate of 1 $^{mm}/_{min}$. For the calculation of the maximum tensile stress, in order to get a better comparison due to thickness variations, the fibres' diameters were determined using a laser confocal microscope assuming a circular cross section. The fibres were then fixed onto a supporting paper frame with a gauge length of 40 mm. Once the fibres were clamped in the testing machine, the paper frame was cut before testing to eliminate this support.

3.2. Polymer characterisation

The mechanical properties have been determined using tension and Charpy impact testing methods. The quasi-static behaviour has been measured via tensile test in accordance to ISO 527-1. Experiments have been carried out on a universal testing machine (walter+bai AG, Switzerland), using a 100 kN load cell. The tensile elongation has been measured with a clip-on extensometer.
The impact performance was measured via Charpy analysis in accordance to ISO 179-1 using an non-instrumented Charpy impact testing machine. To determine the energy absorbed by the specimens, the difference in the potential energies of the pendulum hammer before and after the impact was calculated using the measured hight. In our tests, the machines friction was taken into account, determined by a specimen free test. Both unnotched and notched specimens were tested. The v-shaped notches were introduced with a sharp blade that has the geometry to generate notches in accordance to the testing standard. Five samples of each matrix candidate were tested for both notched and unnotched measurements. The energies absorbed by the specimens were measured using a pendulum with a capacity of 7.5 J.
The entire mechanical tests were carried out on shouldered testing specimens according to ISO 527-1, which had been produced by injection moulding.

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3.3. Composite characterisation

Flexural composite properties (modulus and maximum stress) were determined via three point bending measurements in accordance to ISO 14125. The experiments have been carried out under consideration of the effect of the performed fibre surface treatments on the mechanical properties. Tests were conducted using samples with longitudinal (0°) and transverse (90°) fibre orientation. Therefore, a universal material testing machine (walter+bai AG, Switzerland) was used. The forces were recorded by a 1 kN load cell. The flexural deflection was measured via an external linear variable differential transformer (LVDT).

4. Results and Discussion

4.1. Fibres

Single ampUD flax fibres have been tested in tension to characterise the mechanical properties. The recorded force was referred to an average value of the fibres cross-sectional area calculated using the optically measured diameter. The nominal diameter of an elementary fibre of an ampUD fabric is approximately 20 μm.
The stress-strain curves obtained from tensile tests along with the characteristic properties measured of single yarns are shown in Figure 1 and Table 1, respectively.

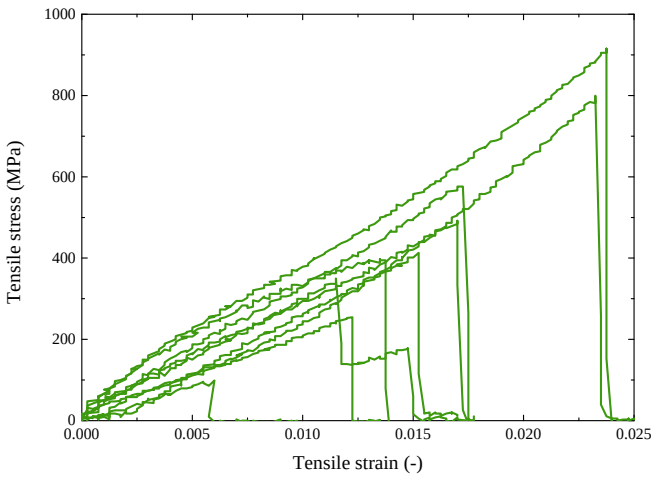

Figure 1: Stress-strain chart of ampUD single fibre tensile testing

Table 1: Tensile properties of ampUD single fibres

	E_{ten} (GPa)	σ_{max} (MPa)	ε at σ_{max} (%)
AmpUD	41.13 ± 6.89	524.77 ± 213.41	1.55 ± 0.54

Tensile tests with the used clamping length led to a mean Young's modulus of 41 GPa for ampUD single fibres, having an acceptable standard deviation. When elevating the clamping length, the modulus can be increased due to a smaller influence of clamping slippage. When analysing the obtained strength values, one can see a fairly high scatter of about 213 MPa. High deviations, especially for the strength, have been reported previously, likely to result from geometrical and structural variations of the fibres [6–8].

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Another possible reason may be due to difficulties in determining the fibre dimensions [9].
The mean values obtained (see Table 1) correlate well with tensile properties provided in literature [2, 7]. However, properties may vary considerably due to comparatively large variations in fibre size along the longitudinal axis along with seasonal deviations. Since natural fibres have a highly complex hierarchical structure, starting from the micro-fibril (⊘ 4–10 nm), over the elementary (⊘ 10–20 μm) and the technical fibre (⊘ 50–100 μm) up to the flax stem (⊘ 2–3 mm) [8], the strength is highly dependent on the size. Whilst elementary fibres yield the highest stress values (clamping length of 3 mm), technical fibers' properties are being reduced with increasing gauge length. However, starting at a clamping length of 25 mm, no further reduction could be recorded with increasing clamping length. The underlying mechanism is the structure of technical fibres composed of short elementary fibres being glued together by pectin. At larger clamping length, it is more likely that failure occurs in the weaker pectin interphase, explaining the constant strength once the clamping length exceeds the length of the elementary fibre [10].
As shown in the stress–strain chart (Figure 1), an initial and irreversible deformation in the low-strain part could not be reported. Andersons et al. [11] attributed such a behaviour to the alignment of the fibrils along the axis of the fibre under load. However, a tensile behaviour as it has been reported for example in [1, 12] which can be classified into three distinct parts (a first linear part, a second non-linear part and a final linear part) was obtained.

4.2. Polymers

Within our study, the tensile and the Charpy impact properties of the pure matrix materials were measured. The tensile stress–strain curves are shown in Figure 2a and the characteristic values, i.e. Young's modulus, tensile strength and strain at maximum stress are summarised in Table 2.

Table 2: Tensile properties of coPOM and referencing materials

Polymer	E_{ten} (GPa)	σ_{max} (MPa)	ε at σ_{max} (%)
coPOM	2.72 ± 0.07	62.94 ± 0.33	9.45 ± 1.29
PP	1.66 ± 0.16	34.79 ± 0.49	8.95 ± 0.87
PLLA	3.54 ± 0.03	69.45 ± 0.62	2.38 ± 0.08
Epoxy	3.48 ± 0.19	63.41 ± 3.64	3.8 ± 0.02

It is shown that the reference polymers (EP and PP) have considerably different properties, whereas both the materials' strength and the elastic modulus are significantly higher for EP. The PP offers due to the lower stiffness, a higher toughness and thus the strain at failure is about four times higher. CoPOM offers similar load bearing capabilities (maximum stress) compared with EP, yet with a significantly higher elongation ability prior to breakage. PLLA yielded similar strength values compared with EP. However, at the same time, the maximum stresses of the PLLA specimens were reached at significantly lower strains. The recorded strain to failure is at 2.5 % which correlates well with literature [13, 14].
Amongst the quasi-static mechanical behaviour, the impact properties are of particular interest. The inherently high toughness may be an added value to the composites which differentiate thermoplastic composites from their thermosetting counterparts. Figure 2b shows the obtained mean values out of five specimens of the different matrix materials and compares the characteristics of unnotched and notched coupons. Epoxy as highly cross-linked material is known to be brittle compared to thermoplastic materials and thus has a low unnotched impact strength of about 28 kJ/m². Although, PLLA is a thermoplastic material, its comparatively high brittleness led to impact strength slightly lower than that of

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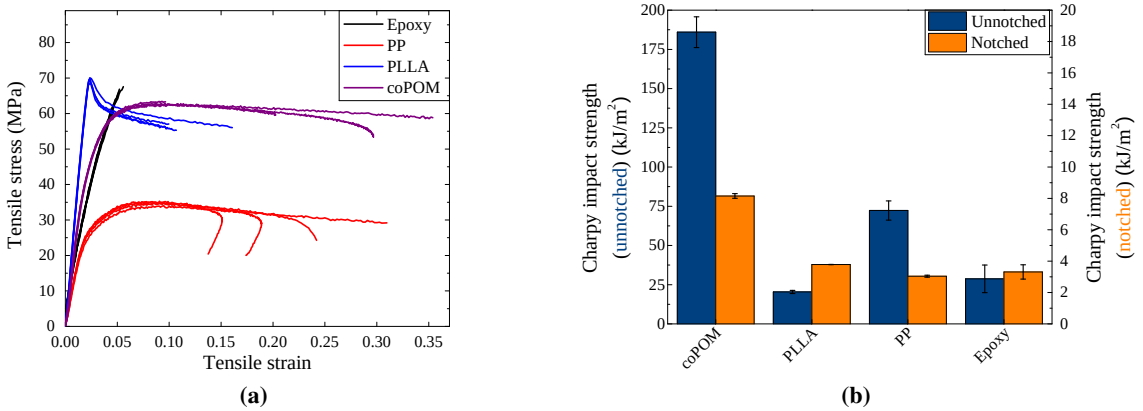

Figure 2: Mechanical properties of matrix materials: (a) Tensile stress–strain diagram and (b) Charpy impact strengths of unnotched and notched specimens

epoxy. PP yielded a three times higher unnotched impact strength than epoxy and PLLA. The attractive price-performance ratio and the comparatively good impact performance affirms the wide use of PP in natural fibre composite applications. In general it can be stated that the fracture behaviour and the impact strength are highly dependent on the polymer characteristics such as molecular mass along with its distribution, the processing induced morphology and, for semi-crystalline materials, the crystalline structure. CoPOM is a polymer which has a high degree of crystallinity and thus reached a more than two times higher impact strength than PP. The difference in the fracture behaviour between PP and coPOM may be attributed to the localised shear yielding of PP which occurs relatively early when exposed to impact loading. Such shear yielding phenomena are predominantly initiated in the vicinity of crystalline areas, promoted also by micro-defects as a result of the volumetric shrinkage during crystallisation [15].
When analysing the notched samples (Figure 2b), one can see that the overall trend has changed. The tests revealed that EP and PP have similar notched impact strength of 3.3 and 3.0 kJ/m^2, respectively. The coPOM specimens yielded strength values which are still considerably higher compared to PLLA (almost three times), yet could maintain just about 4 % of its unnotched load bearing capability. PLLA, in contrast, exhibited the lowest reduction (18.5 % of the unnotched strength), whereas EP could retain 11.5 %. Based on these results, it can be concluded that, despite the low unnotched strength of PLLA, its notch sensitivity was found to be the smallest. However, the coPOM showed still a more than two times higher Charpy impact strength than PLLA.

4.3. Composites

Figures 3a and 3b show the longitudinal and transverse flexural stress–strain charts for ampUD/coPOM specimens possessing either untreated or physically treated fabrics. For each material configuration, a representative curve has been plotted to depict the effect of the plasma fibre surface treatments. Figure 3a points the increase of the longitudinal strength when using the treated fabrics, whereas a significant enhancement of the elastic modulus could not be observed. Further, the strain at maximum stress has not changed remarkably for neither of the modified fabrics used. Interestingly, although tests in longitudinal direction are highly dominated by the fibre properties, an elevated strength could be recorded.
The stress–strain curve of the specimens tested in transverse direction (Figure 3b) show that the strength values could be improved in a similar manner when using the fibre surface treated fabrics. Thereby, the AP plasma treated fabrics revealed superior properties to the LP plasma fabrics. In addition, the AP plasma fabrics could maintain the stiffness, whereas the composites with the LP plasma exhibit a reduc-

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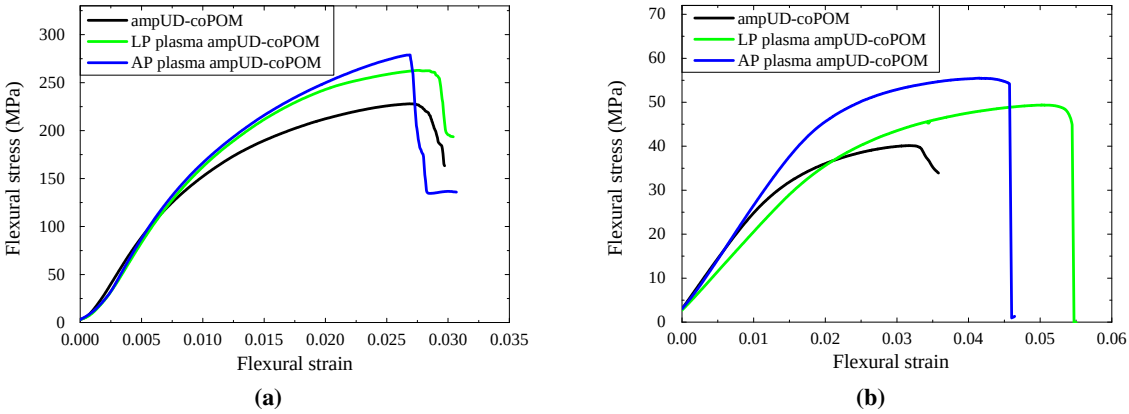

Figure 3: Stress–strain chart of flexural three-point bending specimens tested in (a) longitudinal and (b) transverse direction showing one representative curve for each configuration tested

tion of the elastic modulus. However, a significant increase of the strain to failure could be observed for composites with either of the fibre surface treatments.
Generally, transverse composite properties are more interesting when assessing the quality of the fibre/matrix interface properties [16]. In transverse direction, the properties are dominated by the matrix and the fibre/matrix interface. Thus, variations in the mechanical performance which may be caused by altering the fibre surface, can be rather attributed to either the matrix or the interface and hence to fibre/matrix adhesion.

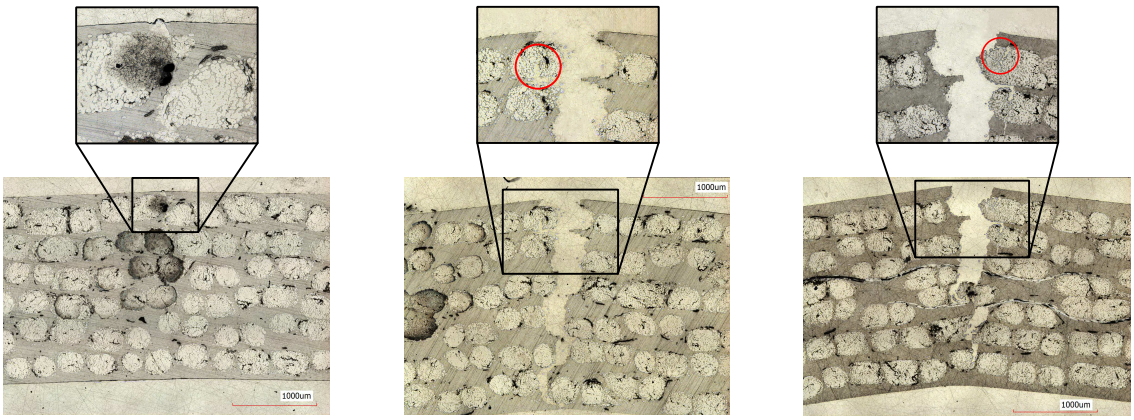

Figure 4: Difference in the transverse flexural failure mode of (a) untreated, (b) low pressure plasma and (c) atmospheric pressure plasma treated flax fibre/coPOM composites; red circles in the close-up views are indicating the partial fibre bundle debonding

Besides the improved properties, a change in the failure mode could be observed. In Figure 4 fracture zones of failed transverse specimens are shown. The pristine specimens tested show very little damage without an obvious crack evolution, whereas the samples with the treated fabrics exhibit distinct cracking. When looking at the failure pattern of the pristine specimens Figure 4a, one will notice the crack

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path along the fibres, whereas the fibre bundles themselves seem to be undamaged. Hence, it can be concluded that the specimens failed rather because of a fibre/matrix interface debonding, whereas the pectin, holding the technical fibres together, could remain intact.
When analysing the fracture pattern of the composites possessing the treated fabrics, the main governing mode is fibre bundle/matrix debonding. However, less bundles next to the fracture surface could maintain integrity. Thus, it can be assumed that the specimens failed by a combination of fibre/matrix interface failure and exceeding the fibres' transverse strength. The damages in Figure 4b and 4c were most likely initiated at a fibre/matrix interface in the vicinity of the convex curved tensile surface. The fairly large damage zones were created rather quick accompanied by a sudden load shedding, which can be also seen by means of the sudden load drops in the stress–strain chart for both fibre surface treatments.

5. Conclusion

Within this study the mechanical behaviour of flax fibres (FF), several matrix materials and their composites have been investigated. The polymers were investigated with an emphasis on polyoxymethylene-copolymer (coPOM) which has not been used in natural fibre composites before, to our knowledge. Further, the effects of a low pressure and an atmospheric pressure plasma treatment on the mechanical performance of FF/coPOM composites were studied.
The following topic related conclusions can be drawn:

(1) Tested flax fibres reached in mean a high specific stiffness with a small standard deviation. The specific Young's modulus is similar to that of E-glass fibres. In terms of the fibre's strength, glass fibres are superior (up to 30 % when comparing to technical flax fibres).

(2) CoPOM has been identified as a novel matrix system for NFC, with added value such as high strength and stiffness along with high toughness.

(3) Fibre treatments, leading to changed chemical composition and morphology of the surface can enhance the adhesion between the hydrophilic natural fibre and a hydrophobic thermoplastic matrix. The impregnation of the tows may be improved in a similar manner. The two plasma treatments performed yielded better mechanical properties in both longitudinal and transverse direction. Particularly, elevations in the longitudinal and transverse strengths along with an increase of the transverse strain to failure could be recorded. This may be caused by an increased bonding strength and/or a better wettability leading to a favourable impregnation.

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