

Starch Acetate N-Fibre Composites

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Abstract

Cellulosic fibre composite compounds based on hemp and flax fibres in triethyl citrate plasticised starch acetate were prepared by melt processing. Composites were prepared with fibre contents up to 50w%. A stiffness of 8.3 GPa and stress at maximum load of 51 MPa were obtained with 40w% flax fibre in a plasticised starch acetate with 20w% triethyl citrate. An almost linear relation between fibre content and the tensile properties was found. The impact strength of the composites was increased with the plasticiser content. The porosity content was low even at high fibre content.

Keywords: Cellulosic fibres; Bast fibres; Mechanical properties; Injection molding; Starch acetate

1 Introduction

An increasing interest in the use of bio-based and biodegradable plastics is motivated by both the ecological concerns as well as the increasing price of oil and petrochemical-based polymers. Besides these external reasons, the materials offer several property related benefits that support their introduction to the daily products of our lives. There are bioplastic applications requiring fibre reinforcement as well as those that need only the neat polymer, just as with petrochemical-based polymer applications. The natural abundance and renewability of cellulosic fibres and starch polymer (among other biopolymers) are the original motivation for the investigation of their suitability in common products. Unlike most fossil-based fibre-reinforced polymers (such as glass fibre/polyester composites), bio-based composites can be disposed or recycled by composting. If incinerated, they typically have much lower ash production than the fossil-based composites [1].

The three main flaws of biopolymers in general and starch in particular are the sensitivity towards water, the brittleness and the low heat stability. Approaches suggested to overcome these three obstacles include the hydrophobic modification of the polymer (eg acetylation of starch), the use of plasticisers and polymers blends, and the reinforcement with fibres. The starch acetates (SA) prepared by acetylation of the free hydroxyl groups of the starch with the degree of substitution (DS) from 0 to 1.0 are water soluble, but above DS 2.0, the internal hydrogen bonding is strongly reduced and the material becomes melt processible [1]. DS is the average number of hydroxyl groups being substituted per monomer unit. The theoretical maximum DS for glucose in starch is 3.0, ie the number of available hydroxyl groups in glucose is 3. The acetylation of starch makes the material less brittle by decreasing the modulus, and by increasing the elongation at break and the impact strength. To further improve the processability SAs are typically plasticised to bring down the glass transition temperature (T_g). Plasticising

can be done by internal or external plasticising agents. In internal plasticising, the hydroxymethyl groups of native starch are substituted by longer alky chains such as hydroxypropyl or the like, reducing the crystallinity and lowering the T_g . External plasticising is based on similar mechanism, but there is no covalent bond between the plasticiser and the starch polymer chains. Triacetine (TriAc) and triethyl citrate (TEC) can be used for this purpose [2]. Native starch can also be plasticised with *eg* water, sorbitol, glycerol and urea for better processability and improved impact strength, however resulting in no improvement in the sensitivity to water. The correct amount of plasticiser depends on its chemical composition. When the plasticiser content is higher than the equilibrium (the highest amount of plasticiser the polymer can withhold), phase separation occurs and the tensile properties quickly deteriorate. *Eg* when using water with native starch, the equilibrium water content is 22% [3]. The plasticising effect of water is based on its hydrogen bonding capability with the native starch. However, when using TEC, with a weaker intermolecular interactions to the SA, the equilibrium content is not associated with that sharp threshold and a gradual change in mechanical properties is observed along the increased plasticiser content.

The stiffness of bast fibres (*eg* flax and hemp) is in the range of 30-70 GPa and this is comparable with the stiffness of glass fibres (GF) of about 70 GPa [4]. In terms of stress at maximum load, GF perform better: strength of natural fibres is in the range 300-1500 MPa, whereas for GF (E-glass) it is about 2000 MPa [5]. However, cellulosic fibres are about 40% lighter than GF (fibre densities of about 1.5 and 2.6 g/cm³, respectively), giving them potentially higher specific properties. To be able to fully exploit the good tensile properties of natural fibres, good fibre-matrix adhesion needs to be accomplished. It has been reported that incompatibility of cellulosic fibres and SA matrix results to a weak interface between the two composite constituents [6], leading to inadequate mechanical performance. However, even with a SA with DS equal to 2.5, and subsequently good melt processability, every sixth hydroxyl functionality of the native starch starting material is still available for hydrogen bonding with the fibres. Thus, in composites with a SA matrix with this DS, the interactions between the fibres and the matrix will be relatively abundant.

In order to produce a starch acetate based matrix compatible with cellulosic fibres in composites, a series of plasticised starch acetates (PSAs) were prepared with variable plasticiser content from 20 to 35w%. Two kinds of natural fibres, hemp and flax were used at fibre contents ranging from 10 to 50w% in the composite to compare the performance of the fibres and the reinforcement effect. Furthermore, two different native starches with different molecular weights were used as raw material in the acetylation and further plasticisation and composite preparation. This was done in order to quantify the effect of polymer molecular weight on the mechanical properties of the matrixes and the composites. The stiffness, stress at maximum load, and impact strength were determined for the neat PSAs and the composites. SEM analysis of fracture surfaces was performed to evaluate the compatibility between the PSA matrix and the cellulosic fibres, and the dispersion of the fibres in the matrix. Finally, the processability and suitability for sample production of the PSA/cellulosic fibre composite compounds was evaluated by producing a number of demonstrator objects.

2 Experimental

2.1 Materials

2.1.1 Matrix

Amylose rich corn starch was supplied by National Starch, USA (Hylon VII: 62w% amylose: 38w% amylopectin) and by Gargill, USA (Cerestar Amylogel 03003: 65w% amylose, 35w% amylopectin). The acetylation of starch was performed according the method described by Lammers *et al* [7]. The plasticiser triethyl citrate (TEC) (tradename: Citroflex2) was obtained from OneMed, Finland.

2.1.2 Fibres

Hemp and flax fibres with lengths of 10-20 and 4 mm, respectively were used in the composites. The fibres were supplied by Ecotex, Poland. To avoid the need for manual feeding of the fibres, they were pelletised prior to feeding. Contrary to unpelletised fibres, the pellets did not cove in the feeder. The pelletising was done with an Amandus Kahl sieve-squeezer with a 390 mm hole-matrix custom-made for cellulosic fibres. Water was used as processing aid in pelletising and to help produce pellets of about 8 mm diameter. The pellets were subsequently dried in a blow dryer at 90°C to less than 1w% moisture content, in approximately 30 min, and packed in aluminium coated, moisture proof heat-sealed PE-bags.

2.2 Compounding

The plasticiser was added to SA using a liquid pump and mixed with a twin-screw extruder (ZE25x48D, Berstorff GmbH, Hannover, Germany) with modified co-rotating mixing screws. Temperatures from 60°C (the feeding section) to 180 or 200°C (melting zones and the die) depending on the materials were used. Screw speed was 300 rpm.

2.3 Injection molding

The granulates obtained from compounding step were dried in a vacuum furnace at 0.40 – 0.10 bar at 40°C for at least one hour before injection molding. The granulates were injection molded with Engel injection molder (ES 200/50 HL, Engel Austria GmbH, Schwertberg, Austria) into ISO 3167 tensile test specimen with length of 170 mm, and with a gauge area section of 10 mm wide by 4 mm thick by 80 mm long. Applied parameters depended on the composition of the molded material, temperatures being approximately from 130°C to 200°C, pressures from 30 to 80 bars, and post pressures from 10 to 70 bars.

2.4 Characterisation

Prior to mechanical characterisation, the test specimens were conditioned at 23°C and 50% RH for a minimum of five days.

2.4.1 Impact tests

Impact strength of the neat PSAs and the composites were determined by using Charpy Ceast Resil 5.5 Impact Strength Machine and ISO 179 standard with controlled ambient conditions: 23°C and relative humidity of 50%.

2.4.2 Tensile tests

Tensile properties of the neat PSAs and the composites were measured according to the ISO 527 standard, on an Instron 4505 Universal Tensile Tester with 10 kN load cell and 5 mm/min cross-head speed. Strain was measured by an Instron 2665 Series High Resolution Digital Automatic Extensometer. Testing was performed at controlled ambient conditions: 23°C and relative humidity of 50%.

2.4.3 Volumetric composition

Determination of the volumetric composition of the composites consisted in gravimetric measurements of four parameters: (i) density of composites (ρ_c) measured by the buoyancy method (ASTM D792), (ii) fibre weight fraction of composites (W_f) measured by chemically dissolving the PSA matrix with chloroform, (iii) density of matrix (ρ_m) measured on neat PSA samples by the buoyancy method, and (iv) fibre density (ρ_f) measured on fibre samples by pycnometry [8,9]. The volume fractions of fibres (V_f), matrix (V_m) and porosity (V_p) in the composites were calculated:

$$V_f = \frac{\rho_c}{\rho_f} W_f \quad ; \quad V_m = \frac{\rho_c}{\rho_m} (1 - W_f) \quad ; \quad V_p = 1 - (V_f + V_m) \quad (1-3)$$

The dimensions of the samples were about (mm): 20 x 10 x 4. The samples were cut from the central part of the tensile specimens. In one case, to test the uniformity of the composite tensile specimens, samples were cut from the entire length of a tensile specimen. The density of hemp and flax fibres were measured to be 1.55 ± 0.02 and 1.57 ± 0.01 g/cm³ (mean \pm stdv. of four samples), respectively. A constant density of 1.55 g/cm³ for both fibre types is used in the calculations of composite volumetric composition.

3 Results and discussion

3.1 Materials development

3.1.1 Starch

In comparison to Hylon VII, PSAs prepared from Cerestar showed much improved mechanical properties: 0.61 versus 0.15 GPa for stiffness, and 10.3 versus 3.1 MPa for stress at maximum load. Unless otherwise noted, Cerestar is the used native starch material in the present study.

3.1.2 Plasticiser

In Figure 1, the specific volume (*ie* reciprocal of the density) of the PSAs is plotted as a function of the weight fraction of plasticiser. The experimental results can be accurately approximated by a linear relationship.

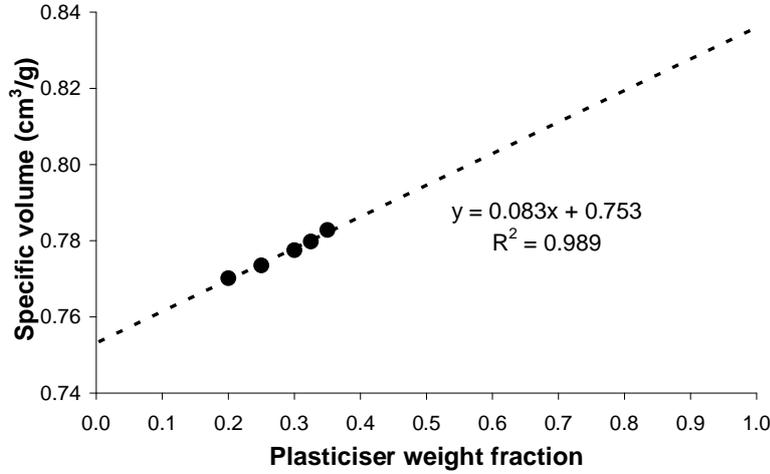


Figure 1 Specific volume (*ie* the reciprocal of the density) as a function of the plasticiser weight fraction of SA compounds. The dotted line is a linear regression line.

Thus, it is shown that the density of the compounds can be calculated by the following equation, which traditionally is used for composite materials with two material constituents (*ie* fibres and matrix):

$$\frac{1}{\rho_{\text{compound}}} = \frac{1}{\rho_{\text{plast.}}} W_{\text{plast.}} + \frac{1}{\rho_{\text{starch}}} (1 - W_{\text{plast.}}) \Rightarrow \quad (4)$$

$$\frac{1}{\rho_{\text{compound}}} = \left(\frac{1}{\rho_{\text{plast.}}} - \frac{1}{\rho_{\text{starch}}} \right) W_{\text{plast.}} + \frac{1}{\rho_{\text{starch}}}$$

where W is weight fraction, and ρ is density.

According to the equation of the regression line in Figure 1, and by using equation (4), the density of neat SA is predicted to be 1.328 g/cm^3 ($= 1/0.753$), which is in good agreement with the experimentally determined value of $1.356 \pm 0.003 \text{ g/cm}^3$ reported in another study of starch acetate [10]. The difference of 0.028 g/cm^3 in the densities is explained by higher DS and lower crystallinity in our material which lead to lower density. Based on the regression lines in Figure 1, the density of neat plasticiser is predicted to be 1.196 g/cm^3 ($= 1/(0.083 + 0.753)$), which agrees well with a density of $1.177 \pm 0.06 \text{ g/cm}^3$ reported for TEC [11]. Based on the measured and estimated densities, the volume fractions of plasticiser in the compounds can be calculated:

$$V_{\text{plast.}} = \frac{\rho_{\text{compound}}}{\rho_{\text{plast.}}} W_{\text{plast.}} \quad (5)$$

where V is volume fraction.

Since the density of neat SA and neat plasticiser are not equal, as estimated above, it follows that the weight and volume fractions of plasticiser in the compounds are not equal. Volume fractions are slightly larger than weight fractions.

Figure 2 shows stiffness and stress at maximum load as a function of the plasticiser volume fraction. The results indicate that the relationship between the tensile properties and the plasticiser content is linear. According to these linear relationships, the tensile properties (both stiffness and stress at maximum load) are approaching zero, when the plasticiser volume fraction is approaching 0.40, which point towards that this is the equilibrium content of plasticiser in the SA. For neat SA (at a plasticiser content of zero), the linear regression lines predict a stiffness of 3.6 GPa and a stress at maximum load of 50 MPa. These tensile property values, typical of a thermosetting polymer such as unsaturated polyester, are a result of highly ordered structure with frequent hydrogen bonds between the carbonyl oxygen acceptors and the hydroxyl as well as the methyl and methylene donors. The introduction of plasticiser increases the degree of freedom for the movement of the polymer chains and renders the material more ductile and less brittle [12]. Even if the linear regression lines in Figure 2 are not reflecting real materials model predictions, they provide good empirical guidelines for the tensile performance of neat PSA compounds; *ie* for a compound with a given plasticiser content, the tensile properties can be calculated from the equations of the linear regression lines.

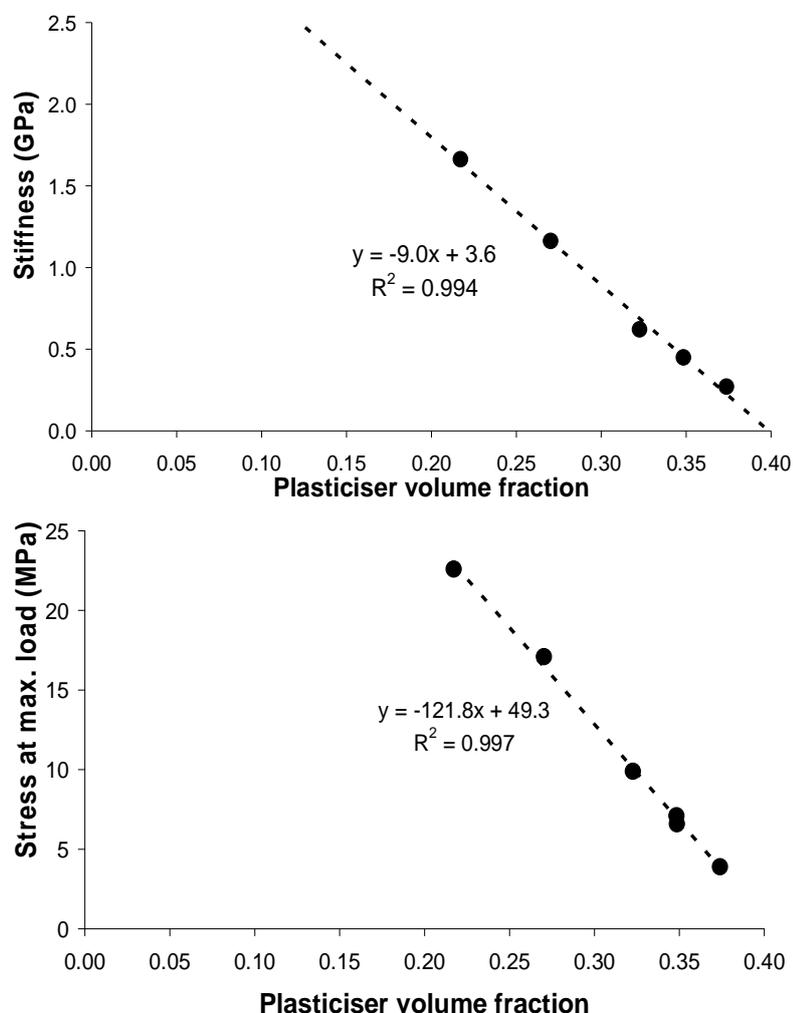


Figure 2 Stiffness (top) and stress at max. load (bottom) as a function of the plasticiser volume fraction of neat PSA compounds. Dotted lines are linear regression lines.

Figure 3 shows the effect of plasticiser content on the mechanical properties of PSA/cellulosic fibre composites. As expected from the results of the neat PSAs, the stiffness and stress at maximum load of the composites are consistently reduced when the plasticiser content is increased. In contrast, the impact strength of the composites is increased with the plasticiser content, and this can be explained by the increased toughness (or ductility) of the composites due to the larger plasticiser content.

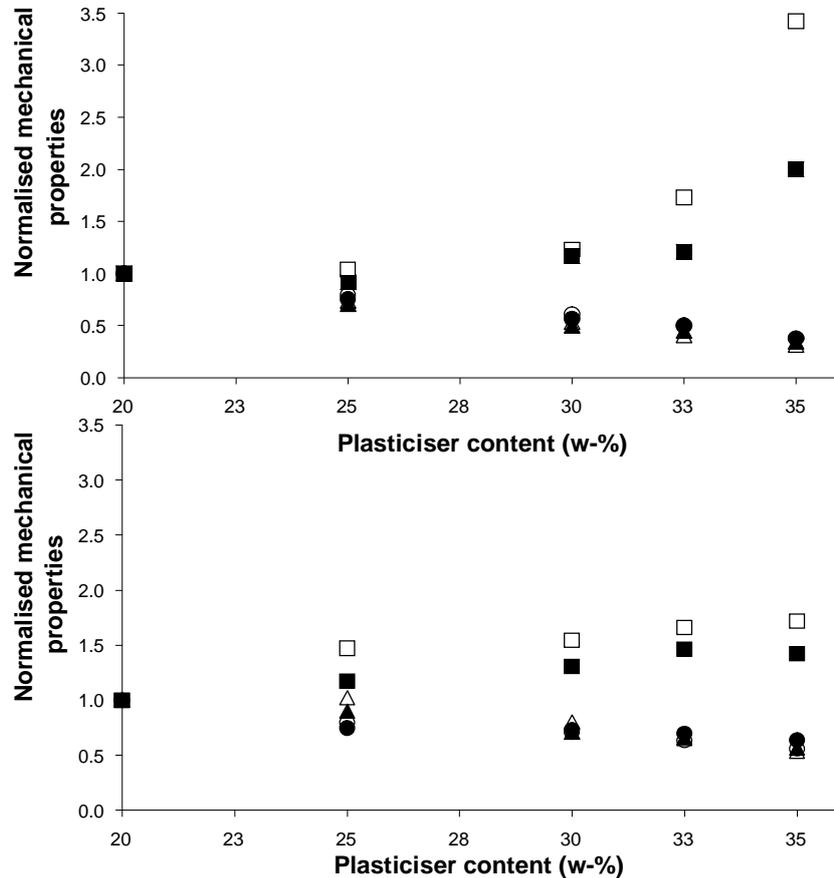


Figure 3 Stiffness (spheres), stress at max. load (triangles) and impact strength (squares) of 10 (top) and 40w% (bottom) hemp (open symbols) and flax (closed symbols) fibre composites as a function of plasticiser content normalised with respect to the 20w% plasticiser content values.

3.1.3 Fibre type and content

There is no clear difference between the mechanical properties of the composite compounds reinforced with the two types of cellulosic fibres. As an example, for PSA1.1 matrix (34.8% TEC) composites with a fibre content of 40w%, the stiffness is 2.4 and 2.7 GPa for flax and hemp fibres, respectively. In another example, the PSA2.1 matrix (20% TEC) composites with a fibre content of 40w% have stiffnesses of 8.1 and 7.0 GPa for flax and hemp fibres, respectively. There seem to be no general and consistent trend that the one fibre type is better than the other for any of the measured mechanical properties. This agrees well with other studies showing that hemp and flax fibres share almost the same chemical composition and mechanical properties [13], and therefore the reinforcement capacity of the two fibre types are similar.

Figure 4 shows normalised mechanical properties of PSA1.1 matrix composites with 10, 20, 40 and 50w% of flax and hemp fibres. Stiffness and stress at maximum load are consistently and almost linearly increased as a function of the fibre content. In contrast, impact strength is less consistently affected by the fibre content; first it is increased when the fibre content is increased from 10 to 20w%, and then it is gradually decreased when the fibre content is increased to 50w%. For these composites, the highest stiffness of 3.6 GPa and stress at maximum load of 21.2 MPa are obtained with the maximum content of 50w% hemp fibres. The highest impact strength of 23 kJ/m² was obtained with 20w% flax fibres. The effect of fibre content on the mechanical properties of the composites will be more thoroughly analysed and discussed in future work.

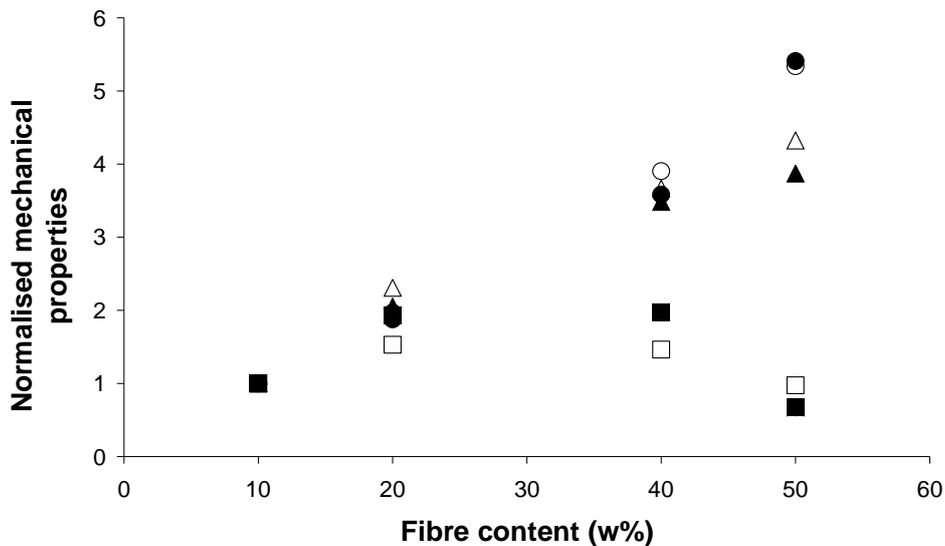


Figure 4 The stiffness (spheres), stress at max. load (triangles) and impact strength (squares) of PSA1.1 matrix composites with hemp (open symbols) and flax fibres (closed symbols) as a function of fibre content. Data are normalised with respect to composites with 10w% fibres.

The better mechanical properties of neat PSA1.2 (34.8% TEC) based on Cerestar starch also resulted in improvement in the properties of the related composites. Stiffness and stress at maximum load of 6.1 GPa and 44.2 MPa, respectively, were measured for PSA1.2 composites with 40w% hemp fibres. In contrast, for composites with the same hemp fibre loading, the PSA1.1 matrix based on Hylon VII starch, only resulted in stiffness and stress at maximum load of 2.7 GPa and 18.2 MPa, respectively. The best tensile performance was observed for composites with PSA2.2 (20% TEC) matrix and 40 w% flax fibers having stiffness of 8.3 GPa and stress at maximum load of 51 MPa. These properties are directly comparable (and even larger) than typical values reported for short fibre composites with a thermoplastic matrix [14].

3.2 Material applications

Boxes with walls of 1 mm thickness and respirator casings with a grid of similar limiting dimensions were injection molded for testing the processibility of the PSA based composite material in applications requiring good processibility and melt flow. Sample specimen of good quality could be produced from these materials. Rectangular beams were produced by profile extrusion of PSA composite compounds with a hemp fibre

content of 60w%. The boxes and respirator casings were molded at Haidlmair GmbH (Austria) and Medop (Spain), respectively. The rectangular profile beams were produced at Maillefer (Finland) with a Conenor Conex Wood Extruder CWE-380-1. The manufacturing chain and the objects prepared in the project are shown in Figure 5.

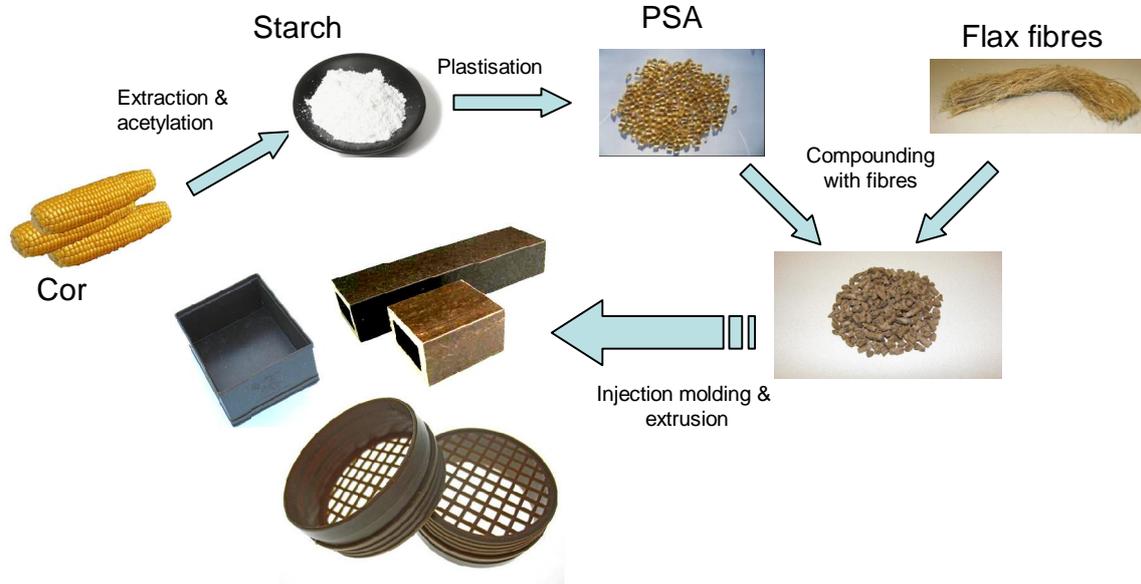


Figure 5 The manufacturing chain for natural fibre composites and sample objects prepared by injection molding (thin walled boxes and respirator casings) and extrusion (rectangular profile). The outer dimensions of the boxes, casings and profiles are (mm): 65 x 100 x 120, 25 x 63 (Ø), and 40 x 80 respectively.

4 Conclusions

Cellulosic fibre composite compounds based on hemp and flax fibres in TEC plasticised SAs were prepared by melt processing. A stiffness of 8.3 GPa and stress at maximum load of 51 MPa were obtained with 40% flax fibre in a PSA matrix with 20% TEC. At low plasticiser content, and high fibre content, materials with good tensile properties were obtained. The higher the plasticiser content, the higher the impact strength. The increase of the fibre content first improved the impact strength, but at higher fibre contents resulted in a reduced impact strength. An almost linear correlation between the fibre weight fraction and mechanical properties was demonstrated. Generally, it was shown that materials with good mechanical properties and good processability can be prepared from PSA/cellulosic fibre composites by melt processing up to a fibre content of at least 40w%.

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