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Influence of Addition of Fiber on the Mechanical Properties of TPS Moldings

Tomasz Oniszczuk, Leon P.B.M. Janssen

Reinforcement by the addition of fibers is common practice in the field of synthetic polymers. When the material is stressed, part of the load will be absorbed by strong fibers, and in this way the strength of the reinforced object can be increased considerably. In the case of biodegradable materials such as thermoplastic starches, it is obvious that the use of biodegradable fibers should be strongly preferable. Fibers for use in common processes such as extrusion and injection-molding are of limited length because of processability. Fibers that were too long would excessively increase the viscosity and moreover would introduce rheopect behavior. The resulting extra increase in viscosity at elevated stresses is unwanted in processing. For the same reason the concentration of fibers is generally limited to 30%. An important parameter in fiber-reinforced materials is the strength of bonding between the fibers and the matrix material. If this bonding is too weak the fiber cannot take up the full force but will be pulled out of the object. This results in a sub-optimal strength.

11.1
Theory of Reinforcements

Optimal biocomposite materials can be processed on standard machines and devices as used in plastics processing [1–4].

The testing of these materials is through test samples: so-called "blades". These blades are subjected to physical and microscopic examination in order to determine the influence of storage, manufacture, and morphology on the quality of a material and its use in packaging production [5, 6]. The microscopic examination is connected with the degree of fiber bonding with the biopolymeric matrix in the vicinity of the area where the sample breaks (Figure 11.1).

The evaluation of the fracture areas consists of evaluating the number of broken fibers and the number of fibers that are pulled out of the matrix. For broken fibers it can be concluded that the bonding is stronger than the fibers themselves, whereas for fibers that are pulled out the fiber strength is superior to the bond strength (Figure 11.2).

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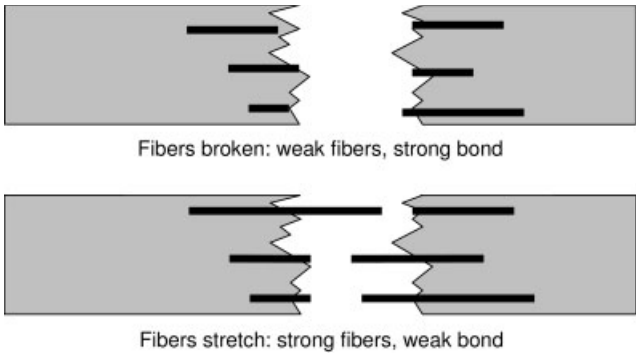

Figure 11.1 The area of biopolymer breakage depends on the degree of fiber and matrix bonding.

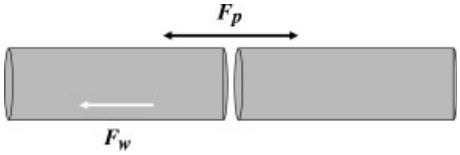

Figure 11.2 Forces acting on fiber during material breakage.

The bond strength between fibers and the thermoplastic starch matrix can be determined as the shear stress (τ) at the interface multiplied by the surface upon which it acts:

$$F_w = \tau\pi\frac{d}{2}l \tag{11.1}$$

where d is the fiber diameter and l is the fiber length.

The force at which the fiber breaks equals the tensile strength of the fiber material (σ_f) times the perpendicular surface:

$$F_p = \sigma_f \frac{\pi}{4}d^2 \cdot [\mathrm{N}] \tag{11.2}$$

Because the fiber will break if $F_w > F_p$ it is possible to define a critical fiber length:

$$l_c = \frac{\sigma_f d}{2\tau} \tag{11.3}$$

In the simplest model it can be stated that if the fibers are longer than the critical length, then fiber breakage will occur, but fibers shorter than the critical length will be pulled out.

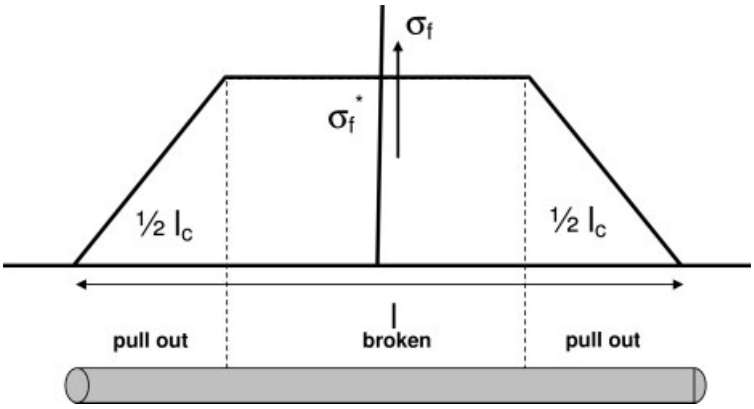

Figure 11.3 Minimal length of pull-out of the long fibers.

In reality, not all fibers will break exactly in the middle. If a fracture in the matrix material encounters the fiber close to one end, pull-out will always occur. If a failure in the matrix material reaches the fiber in the middle region the fiber will break in this middle part, but if it reaches the fiber close to the tip, pull-out will occur if the distance to the tip is in the range smaller than the pull-out length. The total reinforcement of a fiber can now be determined by addition of the contributions of the three regions.

Knowledge of the critical fiber length allows the determination of the number of broken fibers and pull-out fibers in the examined sample. In the case of application of fibers of more than l_c in length, fibers of $1/2l_c$ or more can be pulled out from the starch matrix (Figure 11.3). By macroscopic examination, it is possible to define the number of pull-out fibers versus broken fibers. By determining the pull-out length an indication of the bonding strength between fiber and matrix material can be obtained [7, 8]. For practical situations it can be generalized that if the relative amount of pulled-out fibers is large, improvement of the composite material can be achieved by improving the bonding and by increasing the lengths of the fibers. If, on the other hand, most of the fibers are broken, improvement of strength can only be achieved by using stronger fibers.

11.2 Experimental Data on Fiber-Reinforced TPS

When tests on the strength and bonding of fiber-reinforced composites need to be performed, firstly test bars have to be prepared. The total process consists of two steps. In the first step, starch is gelatinized and mixed with glycerol in an extruder and pelleted. For the experiments with fiber reinforcement the flax or cellulose fibers have to be mixed into the starch during the first process step. The pellets are then very similar to the pellets used in plastic processing and they can

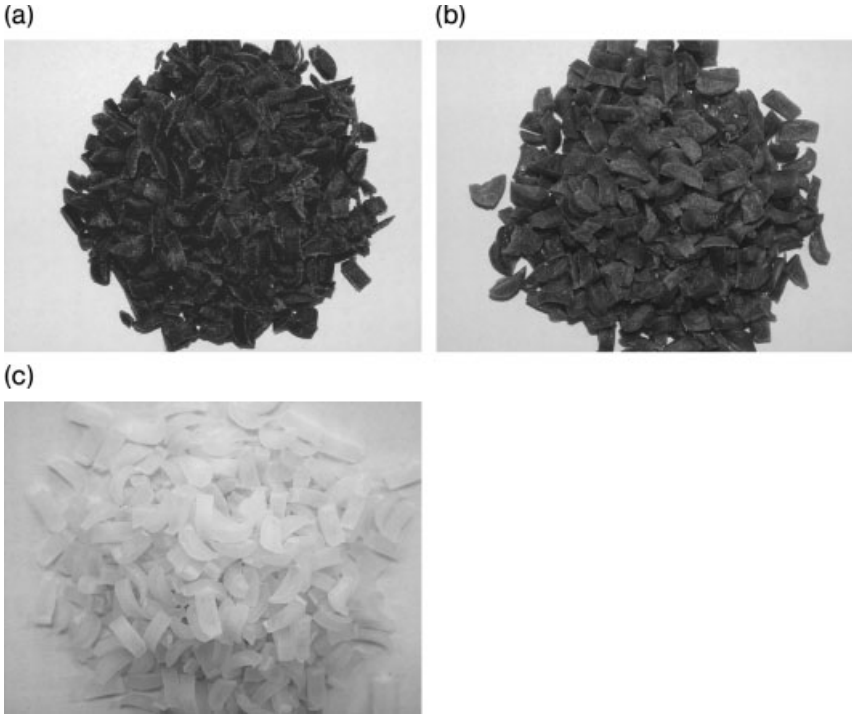

Figure 11.4 Granulates with a) 10% and b) 5% flax fiber content, and c) 5% cellulose fiber content.

be readily fed into the second step, where the product obtains its final shape [6, 13]. This second step is injection-molding (to form three-dimensional objects). Moisture adjustment occurs in the first step, and storage between the first and second production step should be such that this moisture content does not change.

It is advisable that, after mixing, the samples are left in airtight plastic bags for 24 hours in order to allow the intensification of the glycerol penetration into the starch granules. Directly before the extrusion, the mixtures must be stirred again for 10 minutes in order to guarantee a loose and slack mixture structure and to assure a regular feed into the subsequent mixing process.

After extrusion the obtained granulates should be dried in a vacuum laboratory drier at a temperature of 50 °C for 6 hours until a humidity of 4–6% is achieved (Figure 11.4).

As a next step, test bars should be obtained by injection-molding. Production of test bars in the form of a 'spade' is convenient for further examination of mechanical properties. Figure 11.5 shows a mold for the production of various test samples: from top to bottom for notched and unnotched impact strength, for bending tests, and for tensile testing.

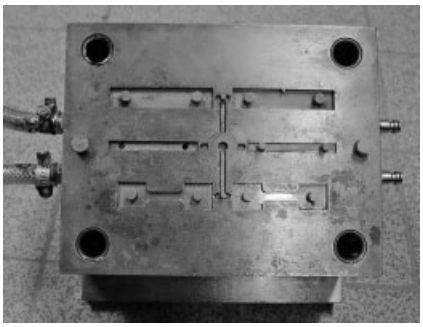

Figure 11.5 Injection mold for the ARBURG 220H90-350 injection machine.

11.3 Critical Fiber Length

In order to define the critical fiber length, it is necessary to know the shear stress (τ) between the fibers and thermoplastic starch. Unfortunately, independent measurement of the value of τ is impossible because of the lack of suitable measurement equipment. Because the problem of determining the value of steady stress between fibers and thermoplastic starch has only recently begun to attract interest, the scientific literature does not provide any definite data; the approximate value of τ was adopted from measurements reported by Morlin and Czigány [8]. In their research, they established that the shear stress between flax fibers and Mater-Bi (which is a variety of thermoplastic starch) amounts to 4.18 MPa.

The mechanical strength of flax fibers varies from 254 to 1100 MPa, depending on the type [9]. From measurements of mechanical features of flax fibers determined on a Wick tester, their breakage strength was established at 663 MPa. Microscopic measurement of the thickness of flax fibers (Figures 11.6 and 11.7) showed an average thickness of 12 μm.

Oniszczuk [6] determined from these results that the critical fiber length for the flax fiber/thermoplastic starch combination is 951 μm.

When performing microscopic examination of the breaking area of a molding, counting the number of the fibers present and measuring their lengths, it is possible to determine the number of broken fibers and the number of fibers that have been pulled out (provided that all the fibers are homogeneous distributed). Because thermoplastic starch with added flax fibers of 4 mm was used during the injection-molding process, the fibers in the breakage areas that have been pulled out are longer than half of the value of l_c: that is, at least 475 μm. Pictures of these fiber measurements are shown in Figures 11.8 and 11.9.

On examination of the samples with 5% flax fiber content, it can be noted that samples with higher glycerol content show shorter pull-out lengths and more breakage. Therefore it can be argued that an increase in glycerol content does not

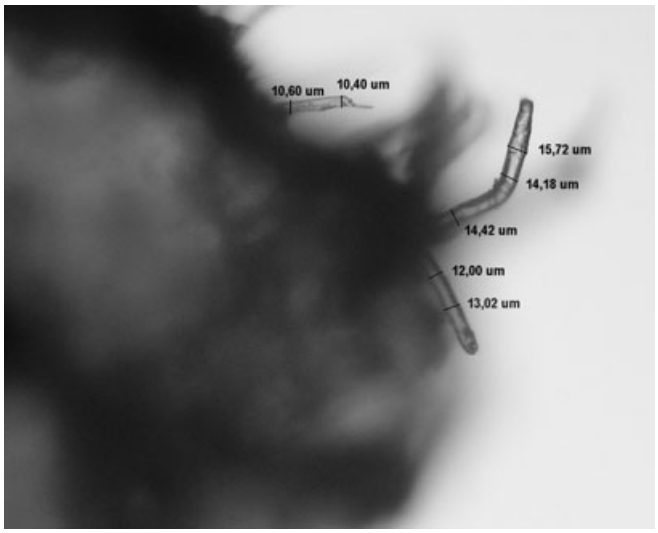

Figure 11.6 The area of breakage of biopolymer molding containing 20% glycerol and 10% flax fibers (fiber diameters).

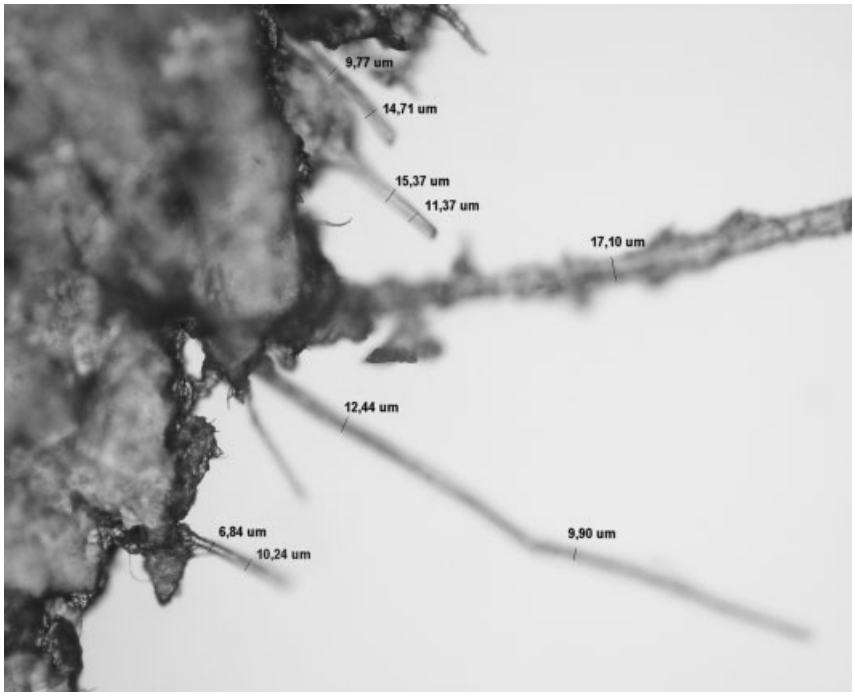

Figure 11.7 The area of breakage of biopolymer molding containing 25% glycerol and 10% flax fibers (fiber diameters).

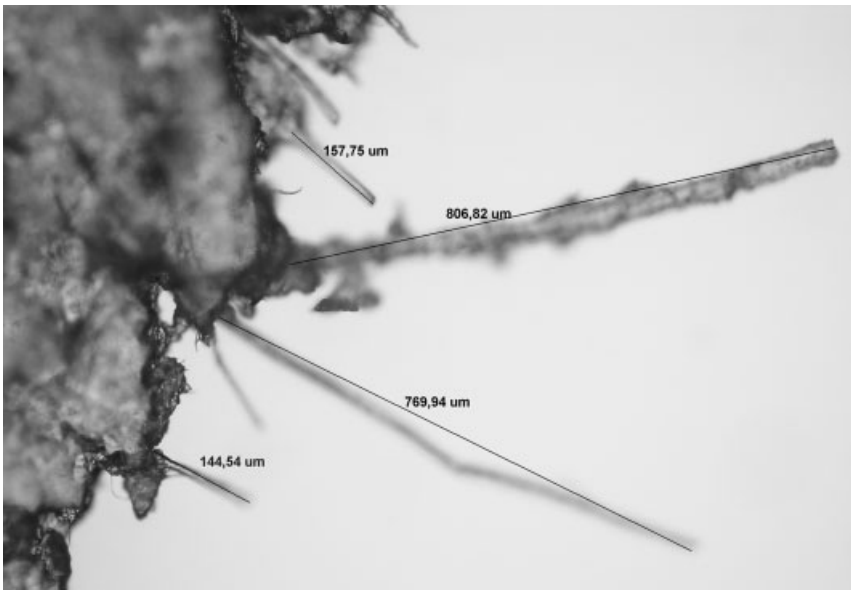

Figure 11.8 The area of breakage of biopolymer molding containing 25% glycerol and 10% flax fibers (fiber lengths).

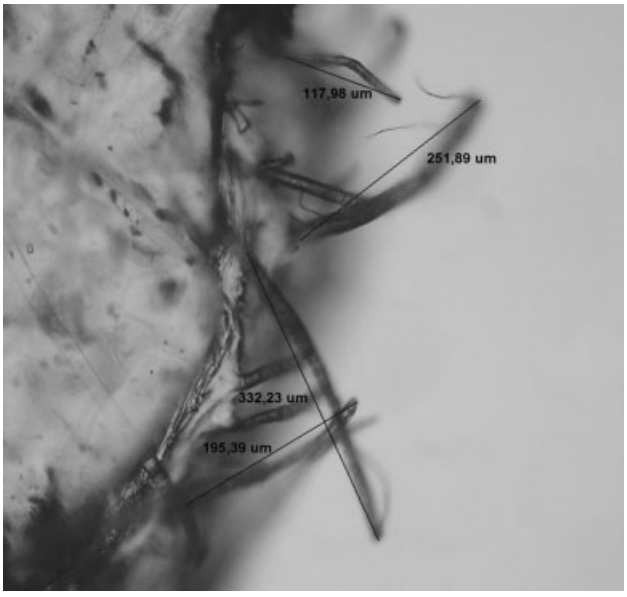

Figure 11.9 The area of breakage of biopolymer molding containing 22% glycerol and 5% flax fibers (length measurement).

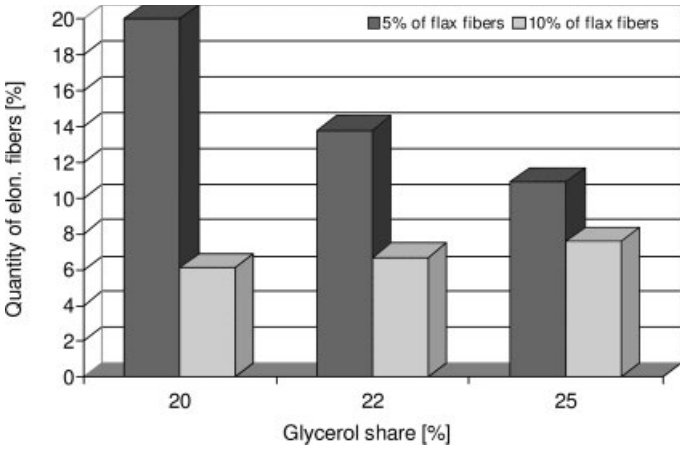

Figure 11.10 Influence of proportion of glycerol on the number of extended flax fibers.

decrease bonding between fiber and matrix material and that a higher plasticity of the starch improves the bonding and the reduced number of pull-out fibers is clearly visible (Figure 11.10). Increasing the glycerol content causes better plasticization of thermoplastic starch, which possibly improves the fiber bonding to the starch matrix through intensified adhesion. An increase in the percentage of flax fibers in the moldings to 10% resulted in enhanced mechanical strength. This might be associated with better fiber bonding with the thermoplastic starch, which is confirmed by the reduced number of fibers extending from the matrix. Nevertheless, the samples displayed a slightly increased number of extending fibers together with the increased glycerol concentration. Probably, despite its improved plasticity due to the presence of the large number of fibers, some proportion of the thermoplastic starch is not involved in the biopolymer matrix structure, which results in the extension of the fibers from the matrix [6].

11.4 Mechanical Properties

The mechanical properties of biocomposites depend on a number of factors. Firstly, these are the quantity and type of fiber added to the material, but the type and amount of plasticizers and the production temperature are also important parameters [14]. One of the parameters with a dominating influence on the mechanical properties of biocomposites is the quantity of both natural fiber and plasticizer [3, 4, 6]. It has been observed that the addition of fiber enhances the mechanical strength. The addition of extra plasticizer causes a decline in the maximum sample stress.

Figures 11.11 show the relationship between maximum stress and flax fiber content in samples containing 20, 22, and 25% of glycerol produced at a material

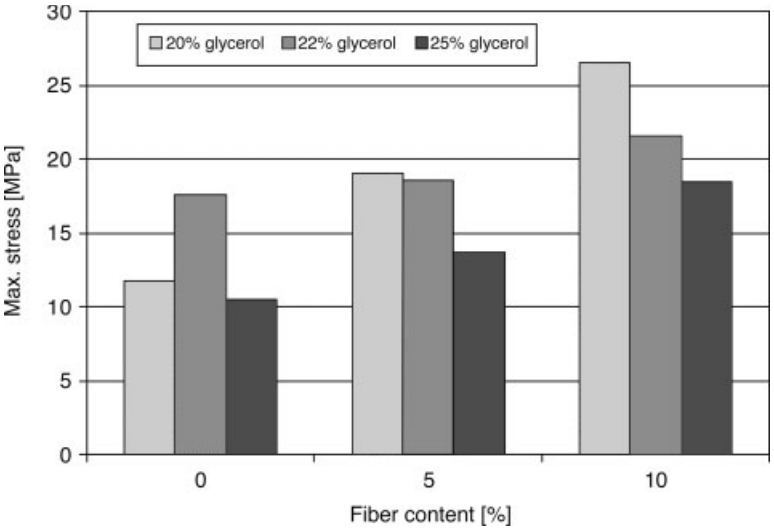

Figure 11.11 Relationship between the maximum stress and the fiber content in samples (sample injection temperature 120 °C) [6].

injection temperature of 120 °C. It is clear that the mechanical strengths of the samples improved together with increasing fiber content.

The samples with 20% glycerol content and 10% of flax fibers showed the highest strength (26.5 MPa). In the case of moldings obtained from granulate containing 22% glycerol, the addition of 5% or 10% of fibers improved the strength slightly. It was noted that in the moldings containing flax fibers the mechanical strength dropped with increasing glycerol content. Glycerol acts as a diluent and weakens the intermolecular bonds between flax fibers and starch [3]. The lowest mechanical strengths were observed with moldings produced from granulates containing 25% glycerol.

The same tendency can be seen in the case of samples obtained at different production temperatures. The highest mechanical strengths were displayed by moldings produced at a material injection temperature of 140 °C (maximal stress 27.8 MPa), whereas the lowest mechanical strengths were noted for moldings obtained at a temperature of 180 °C (10.8 MPa).

Wollerdorfer *et al.* [9] conducted research into the addition of fibers from different sources. They came to the conclusion that there is a considerable influence of the fiber content on the mechanical and strength features of moldings produced from maize and wheat starch in the high-pressure injection process. The use of flax fibers at levels from 10 to 20% considerably improved the mechanical strengths of samples relative to thermoplastic starch without additives. The value of the maximum stress with the addition of 10% of flax fibers was about 20 MPa, the addition of 15% of fibers increased the maximum stress up to 26 MPa, and in the samples with 20% flax fibers the stress was more than 36 MPa.

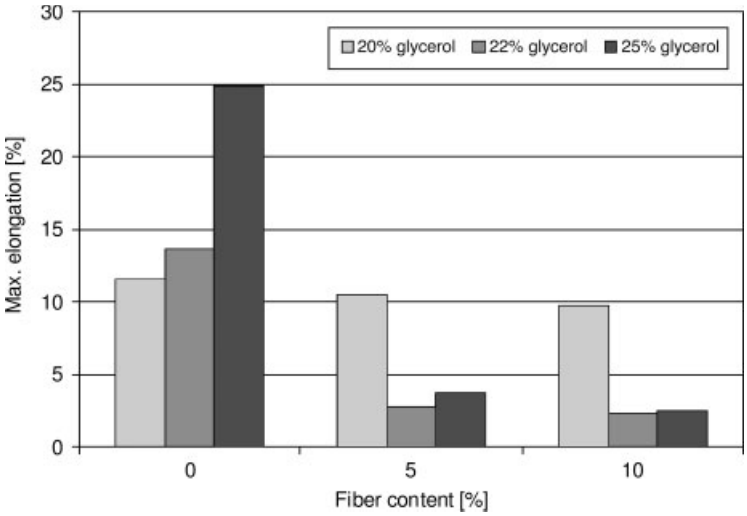

Figure 11.12 Relationship between the maximum elongation and the flax fiber content in samples (injection temperature 120 °C) [6].

Research carried out by Singleton *et al.* [10] into the influence of flax fibers on the properties of HDPE showed that addition of fibers also increases the stress at break in the case of synthetic polymers. The maximum stress was much larger than in the case of thermoplastic starches, due to the different properties of the polyethylene. Without the addition of fibers the maximum stress reached a value of about 27 MPa, and this value could be increased up to 40 MPa by the addition of 30% of flax fibers [10].

In addition, Oksman *et al.* [11] examined the impact of flax fiber on polypropylene (PP) and poly(lactic acid) (PLA), using press-molded stiff forms. The maximum stresses for pure materials amounted to 28 MPa for PP and 50 MPa for PLA. After addition of 30 and 40% of fibers there were slight increases in the stress values, varying from 2 to 5 MPa. This shows that flax fibers have only a minute impact on stresses in PP and PLA [11].

Another important parameter is the maximal elongation of the samples during stretching. For TPS without added fibers, it can be stated that the maximum elongation coincides with increasing injection temperature and with increasing glycerol content in the sample for the full spectrum of injection temperatures and for all glycerol concentrations investigated. The addition of fibers affected the elongation behavior of the material considerably.

Figure 11.12 shows some peculiar behavior. In the TPS with 20% glycerol content the addition of fibers hardly influences the stretching behavior, and the maximum elongation decreases slightly from 10.5 to 9.7%, approximately 10%. In the case of samples with higher glycerol contents of 22 and 25%, the addition of fibers decreases the maximum elongation considerably, although the differences

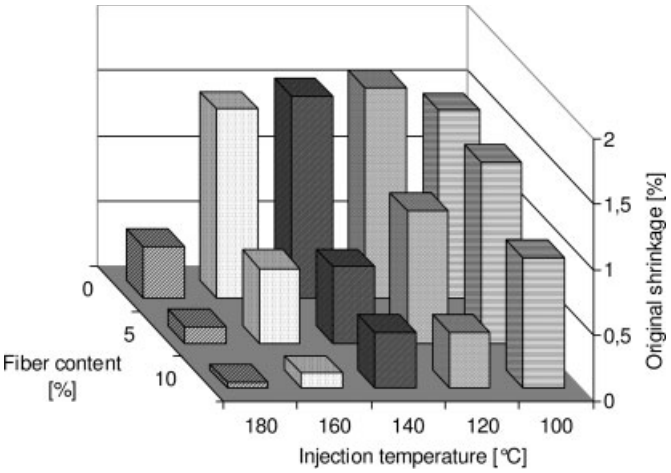

Figure 11.13 Influence of flax fiber content on the magnitude of original shrinkage of moldings (glycerol content 22%) [6].

between addition of 5% and 10% fibers are marginal. When an injection temperature of 180 °C was used instead of 120 °C, the largest maximum elongation (17.1%) was observed with the samples containing 25% glycerol and 5% flax fibers. The lowest maximum elongation (3%) was observed with moldings produced from granulate containing 22% glycerol and 10% flax fibers. Although the underlying mechanism is not yet completely clear, these findings indicate a negative impact of fibers on the flexibility of biopolymer composites.

Similar results were obtained by Wollerdorfer *et al.* [9] when examining starch moldings with the addition of flax fibers, and also by Ma *et al.* [12], who scrutinized moldings enriched with cotton starch.

Besides improving durability, the fibers used for biocomposite manufacture stabilize the shapes and reduce the original shrinkages of ready products. Oniszczuk [6] has reported that an increased linen fiber content will decrease original shrinkage values. The addition of plasticizer (glycerol) had an adverse effect on the original shrinkage.

A very significant parameter determining original shrinkage is the production temperature of the biocomposite. The lowest value of original shrinkage (0.04%) can be observed in samples produced at an injection temperature of 180 °C with granulates containing 10% linen fiber (Figure 11.13). A similar trend is evident in samples produced with 20% and 25% glycerol and 5% and 10% linen fiber.

11.5 Conclusions

Addition of plant fibers to thermoplastic starch granulates positively influences the mechanical strengths of moldings over the entire range of glycerol concentra-

tions. The test bars produced from the granulate containing 10% flax fibers exhibited the greatest mechanical stress.

Examination of the surfaces of moldings with an optical microscope confirmed the lack of changes on their surfaces (cracks, scratches). On analysis of the areas of breakage on moldings, good bonding between fibers and biopolymer was observed in bars with higher glycerol contents, processed at up to 140 °C. Increased fiber content also improves form stability by decreasing shrinkage of the material through the release of internal stresses.

Biocomposites based on matrixes made from biodegradable polymer with reinforcement by natural fibers, such as thermoplastic starch with flax, have great potential as packaging materials of the future [6].

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