STRETCHING OF POLYCARBONATE

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ABSTRACT

By monoaxial stretching, a self-reinforcing effect can be generated in an amorphous PC-film. This self-reinforcement appears in an increase of strength and stiffness as well in stretching as in transverse direction. The mechanical properties depend on the stretching temperature, the stretching rate and the stretching ratio. The forces during stretching can be described by the Poynting-Thomson-Model. Here, the parameter identification depends of the stretching temperature and the stretching rate. In a benchmark, the mechanical, optical and thermal properties as well the raw material prices of conventionally available biaxial oriented films made of PP, PE and PA were compared to monoaxial oriented films made of PC. It was found that monoaxial stretched PC has both excellent properties concerning the mechanical proteries as well as optical properties, haze and gloss.

Index Terms – Polycarbonate, Uniaxial Stretching, Reinforcement

1. INTRODUCTION

Polycarbonate has a great importance in thermoplastic materials due to its unique properties [1]. The market for polycarbonate films has a continuous expansion, which is caused in Asia mainly by the IT industry and label manufacturers as well as in Europe by the automotive industry [2]. The automotive industry mainly used polycarbonate films for decorative applications in interior, such as switch covers, switches and keyboards. Other operations include capacitor films and films for electrical insulation [3].

As polymer components must satisfy ever-growing requirements, methods for optimizing the material-specific properties are necessary. One possibility for refining the polycarbonate film is the monoaxial stretching, which creates a molecular orientation. In this way a self-reinforcement is generated in the film, which is shown by an increased strength and stiffness. Since the self-reinforcement is reached without the addition of reinforcing fillers, monoaxial stretched polycarbonate has a good recyclability [4].

For the stretching of polycarbonate several patents have already been presented in the 70s. Here, semi crystalline polycarbonate cast films, which were made by cast film extrusion, were stretched and thus semi-crystalline polycarbonate films with good properties in stretching direction were prepared. However the results presented here are based on the then current form of to produce semi-crystalline polycarbonate films by cast film extrusion. Amorphous polycarbonate films were produced first in early 90s. Here, no comparable works exist.

Since polycarbonate has high strength, stiffness, impact strength and good optical properties even in its unstretched state, the motivation is to improve these good properties even more by stretching. In this way highly stretched amorphous polycarbonate films with excellent optical properties and even better mechanical properties compared to conventionally available biaxial oriented semi-crystalline films should be produced.

2. FUNDAMENTALS OF STELF-REINFORCED THERMOPLASTIC MATERIALS

Molecular orientation is brought about by moulding processes in the molten state, the entropy-elastic range or the energy-elastic range. This molecular orientation is accompanied by a shape change in the molecules [5]. A force acting from the outside produces deformation and hence causes the macromolecules to line up in the direction of deformation [6]. According to *Ehrenstein*, it is necessary to draw a distinction between reversible and irreversible molecular orientation. Reversible orientation occurs within an individual state range and is reversed once the deformation has been eliminated. Irreversible molecular orientation is all the greater the higher the temperature and the longer the action time. If molecular orientation is introduced at above the glass transition temperature and the polymer rapidly cooled, the orientation will be frozen in and hence become irreversible. The orientation brought about in the material makes it anisotropic, and the strength, stiffness and heat conduction increase in the direction of the orientation, while the thermal expansion und elongation at break are reduced [5]. The molecular orientation is shown in Figure 1.
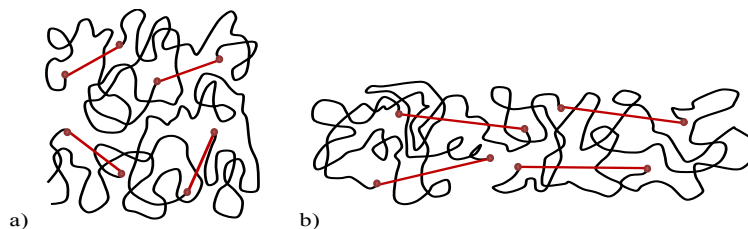
Figure 1: *Schematic diagram of the molecular orientation in polymer materials: a) non-orientated, b) orientated [6]*

2.1 Molecular orientation in the entropy-elastic range ($T_g < T < T_m$)

Above the softening range (T_g) and below the melting range (T_m) is the entropy-elastic (thermoplastic) state range. If a polymer material is subject to tensile loading and stretched in this range, then, under the influence of heat, it will endeavour to contract and become entangled. As long as the elongation is maintained, the reversible orientation can relax through rearrangement of the molecules. The untangling of the molecule chains will thus be all the more complete the higher the mobility of the molecules and the greater the amount of time that is available, i.e. the lower the deformation rate. The reversible orientation generated in the entropy-elastic range, together with the inherent stresses caused by this, become frozen in through cooling to below the softening range and are then irreversible. In this way, the material behaviour becomes anisotropic, i.e. in the direction of orientation, the strength, stiffness and heat conduction all increase, while the thermal expansion the elongation at break undergo a fall. The orientation introduced here is denoted stretching [5].

2.1.1 Monoaxial stretching of amorphous thermoplastics

In amorphous thermoplastics, the secondary valence forces only act at the point where the macromolecules cross each other. Molecular orientation generates anisotropy in the amorphous thermoplastics [6]. The stretching ratio is limited by the degree of molecule entanglement. The material can only be stretched without any suffering damage to the extent that the entanglements permit. During deformation, new tangles develop, while others come undone. This reaction increases as the temperature rises [7]. Figure 2 shows the molecular structure in the non-loaded original state and how this changes when subject to tensile loading. The strain causes the molecule chains to become aligned in the direction of

stretching, with the result that the covalent bonds have the chief influence in this direction. The share of covalent bonds is thus reduced at right angles to the direction of stretching, which means that primarily secondary valence bonds are found at right angles to the direction of stretching [8].
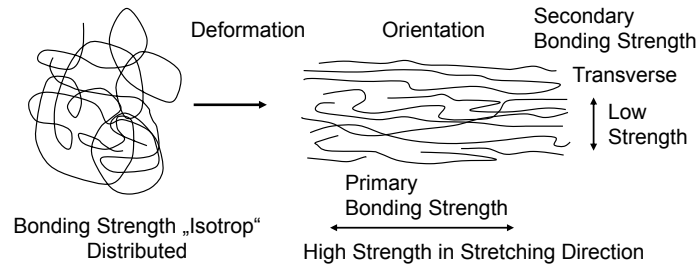
Figure 2: *Macromolecules of an amorphous thermoplastic: with no load and under tensile load [8]*

*2.1.2 Monoaxial stretching of semi-crystalline thermoplastics*
Figure 3 shows how the molecular structure of a semi-crystalline thermoplastic behaves during stretching at just below the crystalline melting point. The deformation initially takes place in the amorphous areas. With an increasing level of strain, the semi-crystalline areas become aligned in the loading direction. If the strain is increased still further, the crystalline areas break up into blocks [9].
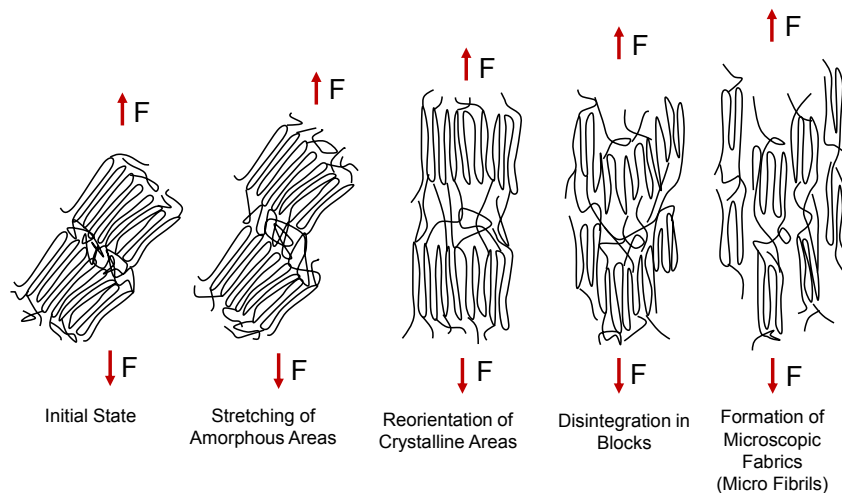
Figure 3: *Stretching a semi-crystalline thermoplastic [9]*

## 2.2 Methods for introducing molecular orientation
The production of plastic products and the implementation of shape changes on semi-finished products are closely linked to the temperature-conditioned state ranges [7]. Figure 4 shows the shaping methods that are feasible within the different state ranges.
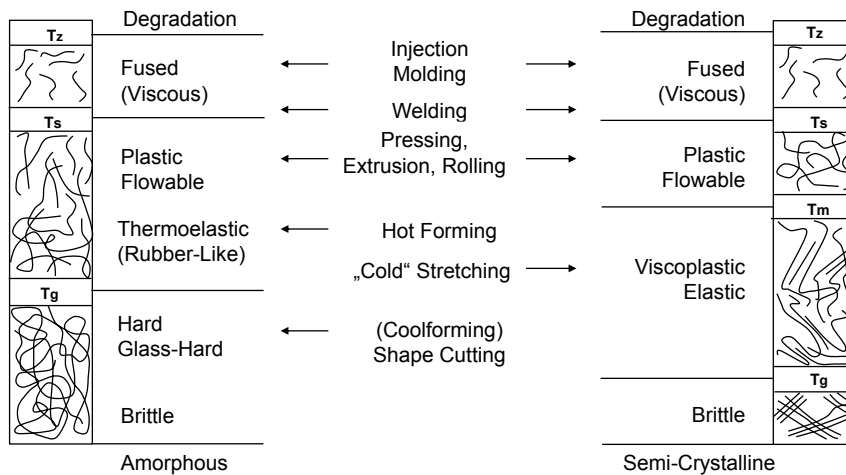
Figure 4: *State ranges and feasible shaping methods for thermoplastics [7]*

3.   MONOAXIAL STRETCHING OF POLYCARBONTE

For monoaxial stretching, use is made of stretching units that apply the necessary tensile stress through a frictional connection on the basis of rotating rolls. Figure 5 shows the structure of a monoaxial stretching unit, which is used here, for stretching in a narrow gap. The unstretched film runs into the stretching unit on the right-hand side and is heated to the required stretching temperature in the heating zone (rolls 1 to 3) and stretching zone (rolls 4 to 6). The film is stretched through the different running speeds of the first and second roll units. Following this, the stretched film passes through the annealing zone (rolls 7 to 9) until it is cooled to room temperature in the cooling zone (rolls 10 and 11) and is wound onto a winder with a defined torque.
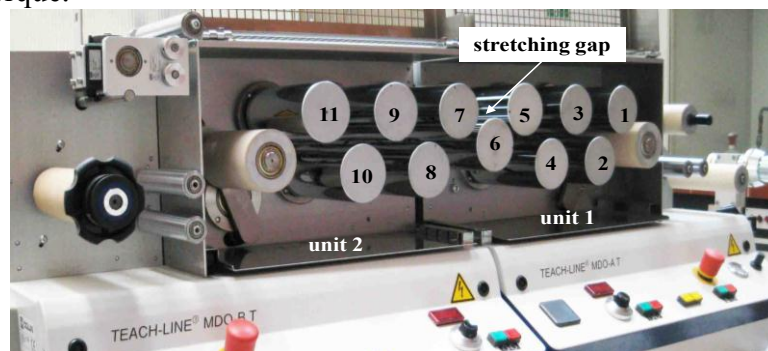
Figure 5: *Monoaxial stretching unit for stretching in a narrow gap*

The temperature profiles are set out in the order in which the film runs through the individual heating and cooling zones. The speed of the first roll unit is designated by variable v_1. Variable v_2 thus applies for the speed of the second roll unit. The stretching ratio (SR) is the quotient of speeds v_1 and v_2.

3.1   Forces during deformation

In order to measure the forces that act during stretching, the polycarbonate film is stretched on a universal testing machine in a hot-air oven.

The tensile test can be applied under following consideration on the stretching process. As shown in Figure 6, an infinitesimal strip is regarded, which is stretched. At the separation

point of roller six (Figure 5), continuously new strips are follow, which are stretched. The process can thus be seen as a tensile test with moving grip. At place of the clamping length (tensile test), an infinitesimal strip is considered.
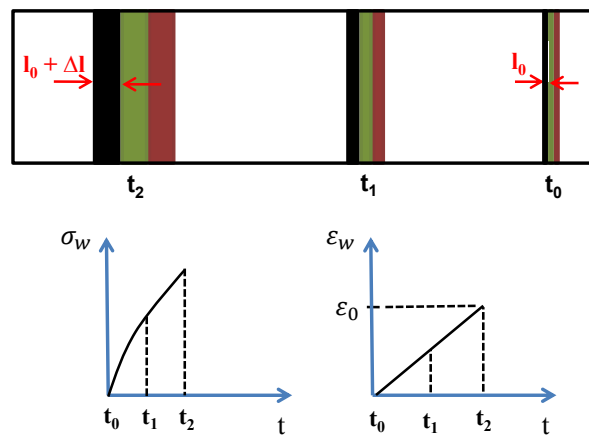
Figure 6: *Description of the stretching process*

Figure 7 shows the curve for the true stress σ over time for 160 °C, stretching ratios of 20 % and 50 % and strain rates of 50 mm/min and 300 mm/min.

After application of the strains, the films were kept hot and the relaxation recorded as the fall in stress over time. The molecules require *"a certain time in order to achieve the deformation that corresponds to the acting stresses through molecular rearrangement"* [10]. The tensile curve increases degressively on account of the viscoelasticity and, as the temperature is kept constant, falls in the form of a decay function (exponential function with negative exponents) to an equilibrium level. It can be seen here that an increase in the strain rate leads to an increase in the stress. The equilibrium stress to which the stress curve falls is a function of the prior strain history.
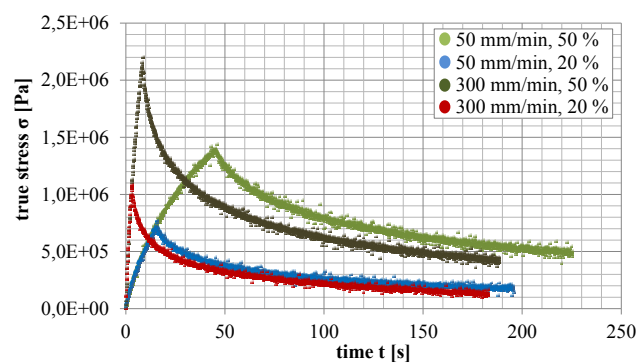
Figure 7: *Influence of the strain and strain rate on the true stress vs. time curve*

3.2 Model for describing the stretching process
The Poynting Thomson model is used to describe the true stress over time [10]. This is a parallel arrangement of a Maxwell model with a spring element (Figure 8).
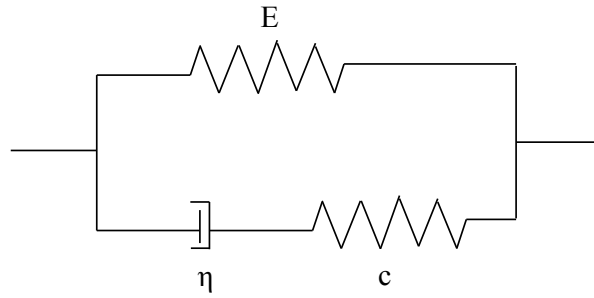
Figure 8: *Equivalent circuit of the Poynting-Thomson-model to [9]*

The model is described by the following differential equation.

$$\dot{\sigma} + \frac{c}{\eta} \cdot \sigma = (E + c)\dot{\varepsilon} + \frac{E \cdot c}{\eta}\varepsilon \tag{1}$$

E and c describe the elastic component (spring) here, ε describes the applied strain and η the viscous component (damper) [10].
Solving the differential equation with allowance for the starting conditions

$$\sigma(0) = 0 \; und \; \varepsilon(0) = 0 \tag{2}$$

produces the following description of the stress curve over time:

$$\sigma(t) = (E + c) \cdot \varepsilon(t) - \alpha c \int_0^t e^{-\alpha(t-\tau)}\varepsilon(\tau)d\tau \tag{3}$$

Where

$$\alpha = c/\eta \tag{4}$$

During stretching, a stressing test is conducted which is divided into two ranges, the tensile test and the relaxation:

$$\varepsilon = \begin{cases} \dfrac{\varepsilon_0 \cdot t}{t_1} & 0 \leq t \leq t_1 \quad Range \; I \\ \varepsilon_0 & t > t_1 \qquad Range \; II \end{cases} \tag{5}$$

Range I: Tensile Test
The following applies

$$\sigma_I(t) = (E + c)\frac{\varepsilon_0}{t_1}t - c\alpha \int_0^t e^{-\alpha(t-\tau)}\frac{\varepsilon_0}{t_1}\tau \; d\tau \tag{6}$$

with the solution

$$\sigma_I(t) = {\varepsilon_0}/{t_1} \left(Et + \eta(1 - e^{-\alpha t})\right) \tag{7}$$

for describing the tensile test.

Range II: Relaxation

Since the integration is performed via the blip at point $t = t_1$ here, it is necessary for the integration to be divided up into two integrals [10]. The following thus applies here:

$$\sigma_{II}(t) = (E + c)\varepsilon_0 - \alpha c \int_0^{t_1} e^{-\alpha(t-\tau)} \frac{\varepsilon_0}{t_1} \tau \, d\tau - \alpha c \int_{t_1}^t e^{-\alpha(t-\tau)}\varepsilon_0 d\tau \qquad (8)$$

with the solution

$$\sigma_{II}(t) = E \cdot \varepsilon_0 + \frac{\varepsilon_0}{t_1} \eta(e^{-\alpha t_1} - e^{-\alpha t}) \qquad (9)$$

Through the experimentally-determined stress curves, it is possible to establish parameters η, E and α. These are shown in Table 1 for 160 °C, a stretching ratio of 50 % and a strain rate of 50 mm/min.

Table 1: *Parameters of the Poynting Thomson model*

|	η [Pa s]	E [Pa]	α [1/s]
160°C_v50_50%	135000000	880000	0,02

In Figure 9, the Poynting Thomson model has been parameterized for a temperature of 160 °C, a strain rate of 50 mm/min and a strain of 50 %. It is shown that the model is capable of describing the degressive curve profile for the tensile range and the decay function of the relaxation range.
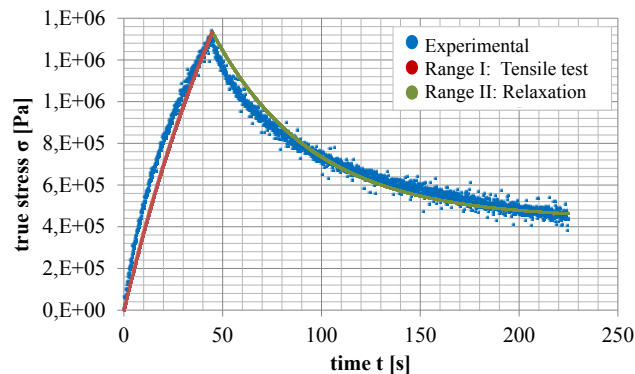
Figure 9: *Parameterized Poynting Thomson Modell for the tensile and relaxation ranges*

3.3 Mechanical properties auf stretched Polycarbonate

An amorphous polycarbonate film is stretched on the monoaxial Tech-Line MDO A / MDO B stretching unit from Dr. Collin that is shown in Figure 5. Figure 10 shows the influence of the heating and cooling in the stretching unit on the mechanical properties, which were measured in tensile tests to DIN EN ISO 527-3. Temperature patterns of 140 °C – 150 °C – 80 °C and 150 °C – 160 °C – 90 °C were selected, and the films stretched with otherwise identical stretching ratios and stretching rates. The tensile strength of the non-stretched polycarbonate film is 60 MPa. A slight increase in strength is achieved by stretching with a temperature of 150 °C in the stretching zone. Stretching at 160 °C, by contrast, leads to a tensile strength of 110 MPa with a stretching ratio of two.
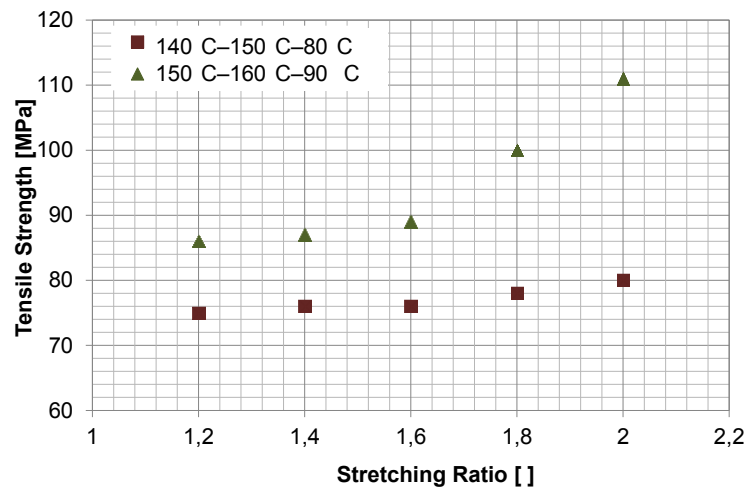
**Figure 10:** *Influence of the temperature control on the tensile strength in the direction of stretching*

The stretching ratio (SR) is observed as a further process parameter, and the stress-strain curve set out in the direction of stretching (Figure 11 a)) and at right angles to the direction of stretching (Figure 11 b)). A higher stretching ratio leads to a higher maximum tensile strength and to a higher stiffness in the direction of stretching. The stress-strain curve remains unchanged at right angles to the direction of stretching.
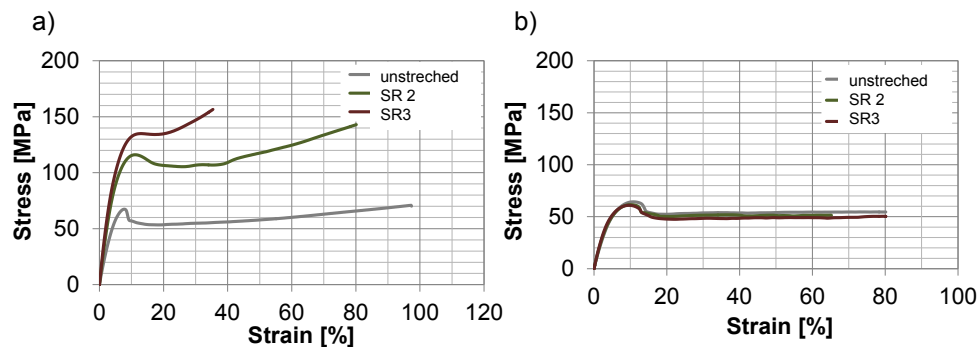
Figure 11: *Influence of the stretching ratio on the stress-strain curve in a) the direction of stretching and b) a right angles to the direction of stretching*

A further process parameter is the strain rate. With a constant stretching ratio of three and a temperature pattern of 150 °C – 160 °C – 90 °C, the stretching rate is varied, and the following stress-strain curves are obtained in the direction of stretching (Figure 12 a)) and at right angles to the direction of stretching (Figure 12 b)). It can be seen here that the stress-strain curve is a function of the strain rate and that, with lower strain rates, higher maximum tensile strengths and stiffnesses can be achieved. An improvement in the mechanical properties is also obtained at right angles to the direction of stretching too on account of the slow stretching.

a)   b)
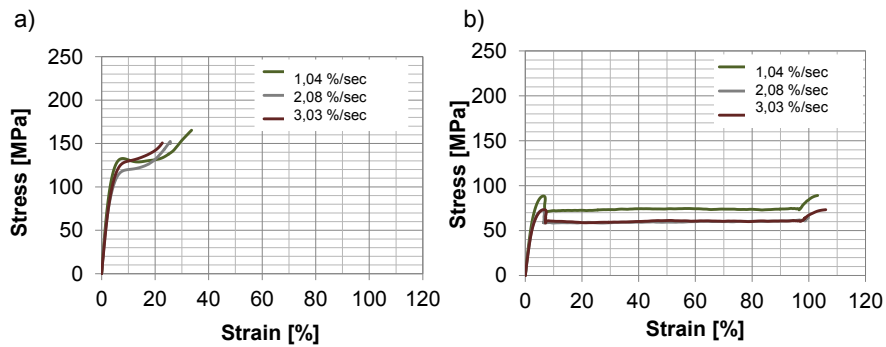
Figure 12: *Influence of the strain rate on the stress-strain curve in*
a) the direction of stretching and b) at right angles to the direction of stretching

Since better mechanical properties are obtained with low strain rates, the stretching ratio is increased with a low stretching rate of 1.04 %/sec, and the following stress-strain curves are obtained in the direction of stretching (Figure 13 a)) and at right angles to this (Figure 13 b)). Here, it is possible to achieve a maximum tensile strength of 183 MPa in the direction of stretching and 91 MPa at right angles to this direction. The stiffness increases to 3300 MPa through stretching in both the stretching direction and at right angles to this.

a)   b)
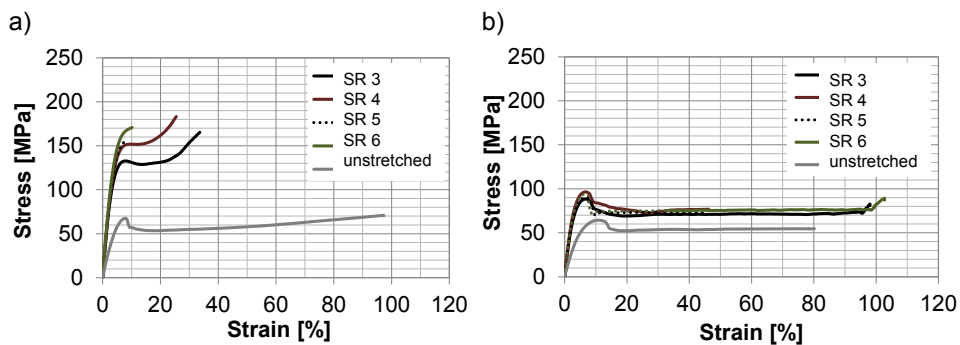
Figure 13: *Influence of the stretching ratio with a low stretching rate on the stress-strain curve in a) the direction of stretching and b) at right angles to the direction of stretching*

It can be stated that the mechanical properties achieved through uniaxial stretching are a function of the stretching temperature, the stretching rate and the stretching ratio and that the orientation that develops leads to an increase in the strength and stiffness.

4.   BENCHMARK

A comparison was made between industrial biaxially stretched films of PP (BOPP), PA (BOPA) and PET (BOPET) and monoaxially stretched PC film (MOPC). The strength, stiffness, impact strength, heat resistance, shrinkage, transmission and gloss of the films were measured and compared. Furthermore, the raw material price was also compared. To determine the strength and stiffness, tensile tests to DIN EN ISO 527-3 were performed. The impact strength was measured in impact strength tests to DIN EN ISO 8256. The heat deformation resistance/shrinkage was examined to DIN 53 497 5C in a hot air oven. The transmission measurement was carried out with a spectrophotometer to DIN 5033. The gloss was measured with a reflectometer to DIN 6750.

Figure 14 shows the measured properties as a comparison. It can be seen here that the MOPC film has both excellent mechanical properties as well as optical properties, haze and gloss.
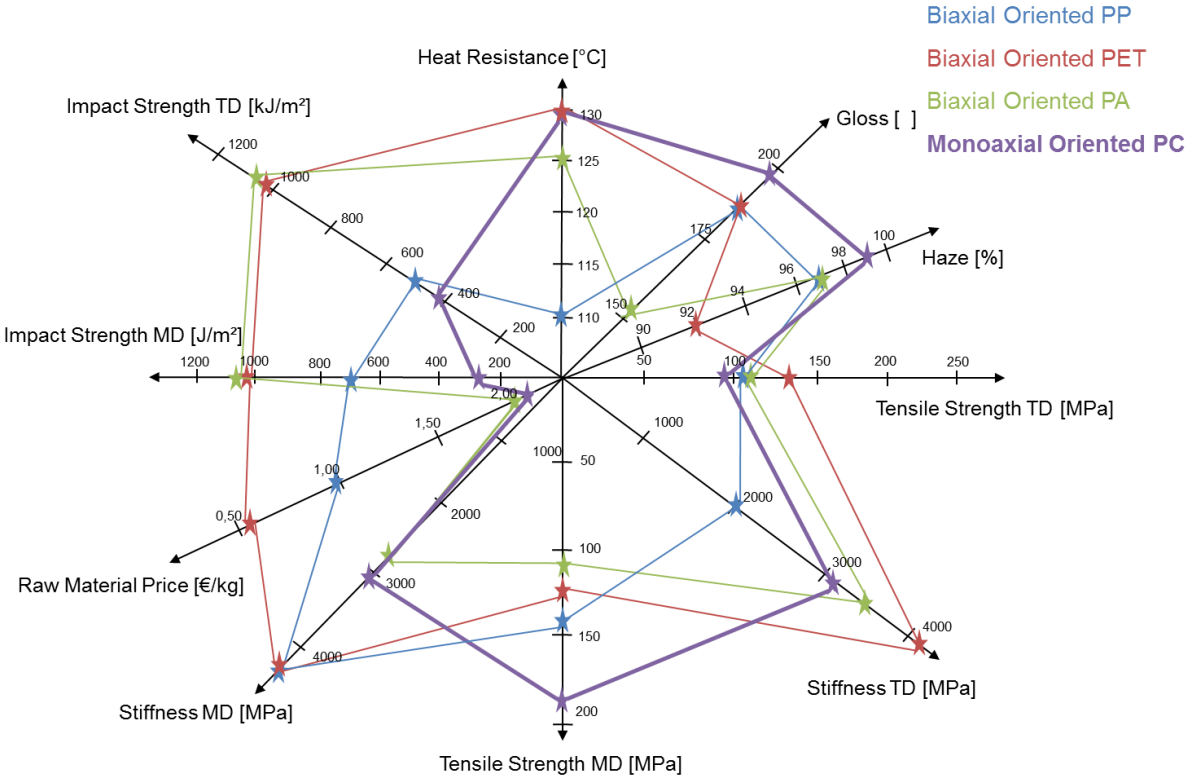

Figure 14: *Comparison of the mechanical, thermal and optical properties*

5. CONCLUSION

By monoaxial stretching a self-reinforcement is generated as well in the amorphous polycarbonate film. Hereby the mechanical properties depend on the stretching temperature, the stretching rate and the stretching ratio. Here, the best mechanical properties are generated at a stretching temperature just above the glass transition temperature, a slow stretching rate and a stretching ratio of four. In this way, the tensile strength in stretching direction increased to 155 MPa, the breaking strength to 185 MPa and the modulus of elasticity to 3.200 MPa. Transverse to stretching direction the tensile strength increased to 90 MPa, the breaking strength to 80 MPa and the modulus of elasticity as well to 3.200 MPa. The forces during stretching were described by the Poynting-Thomson-Model, whose parameters depend on the stretching temperature and stretching rate. In a comparison between biaxial stretched semi-crystalline films made of PP, PA and PET and monoaxial stretched amorphous films made of PC it was found that monoaxial stretched PC has both excellent properties concerning the mechanical properties as well as optical properties, haze and gloss.

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