T. Hentschel, H. Münstedt

Thermoplastic Polyurethane – The Material Used for the Erlanger Silver Catheter

Summary: The Erlanger silver catheter consists of a thermoplastic polyurethane elastomer (TPU). To achieve an antimicrobial effect, silver particles at a concentration of 0.5–1.0% by weight are incorporated into the basic material. The good mechanical properties were shown to remain present after the incorporation of the silver. The characteristic mechanical data of blends made of a soft and a hard TPU type approximated closely to a linear relationship with the ratio of the mixture. The buckling stability of catheters as a function of their cross section could be described by Euler's formula. This enables the buckling stability to be calculated when material constants and catheter geometry are known.

Introduction

Thermoplastic polyurethane elastomers (TPU) combine easy thermoplastic processing and excellent elastomer properties. They possess a rubberlike high elasticity and ductility, a high resistance to abrasion and chemicals and a high tensile strength. The hardness and other mechanical characteristics of TPU are primarily controlled by the chemical composition and can be varied over a wide range [1–4]. For these reasons, many types of clinical catheters are made of TPU.

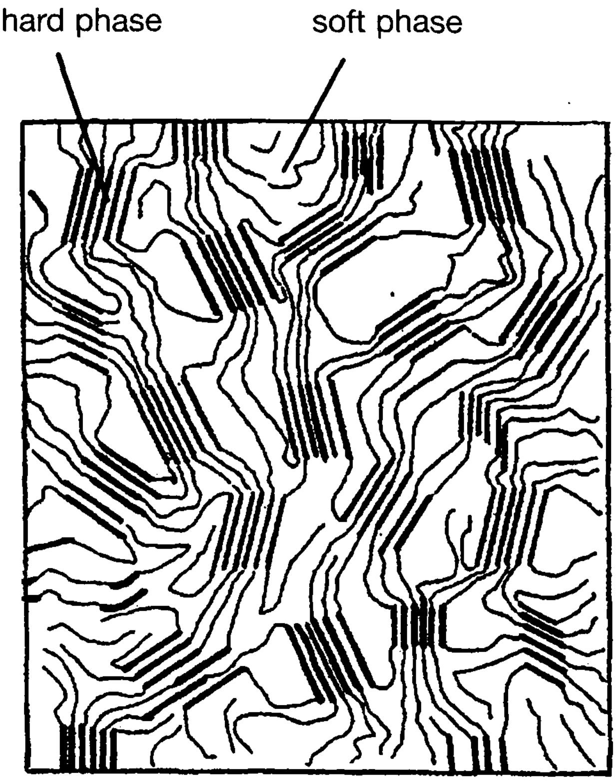

Figure 1: Diagram of the structure of a polyurethane elastomer [5]. The soft phase permits extensive deformability and the hard domains act as physical cross-links that give the material its distinctive elasticity.

TPU are copolymers that consist of two chemically different types of monomer. They are synthesized by means of polyaddition of di-isocyanates and diols. Molecular weights of the macromolecules typically range from 20,000 to 50,000 g/mol. Neighboring molecules can form hydrogen bonds between their characteristic urethane groups. These physical crosslinks force the molecules back to their initial position even after severe deformation and thus give the material its high elasticity. The high ductility of the polyurethane elastomers is achieved by inserting long-chain bifunctional polyols into the macromolecules. Polyols are flexible and form soft segments within the macromolecular chain. The cross-linked regions within a TPU are known as the hard phase and the regions in between, consisting of the polyol soft segments, as the soft phase (Figure 1). The hardness of TPU is primarily controlled by the ratio between the hard and soft phases [1, 2].

The mechanical properties of clinical catheters have to meet a number of critical requirements. The catheters need to be sufficiently stiff to avoid blockage of the lumen or lumina due to buckling. At the same time they must exhibit sufficient flexibility to fit into the vessels in which they are located, and to be well tolerated by the patient. These requirements can differ considerably depending on the type of catheter.

It is particularly important to ensure that the good properties of TPU are not impaired by processing or by additives which are incorporated for specific functions. In the Erlanger silver catheter, silver particles are incorporated into the TPU matrix by means of a complex processing technique. Hence it is very important to compare the properties of the material before and after processing.

Dipl.-Phys. *T. Hentschel*, Prof. Dr. *H. Münstedt*, Institut für Werkstoffwissenschaften, Lehrstuhl für Polymerwerkstoffe, Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstr. 7, D-91058 Erlangen, Germany.

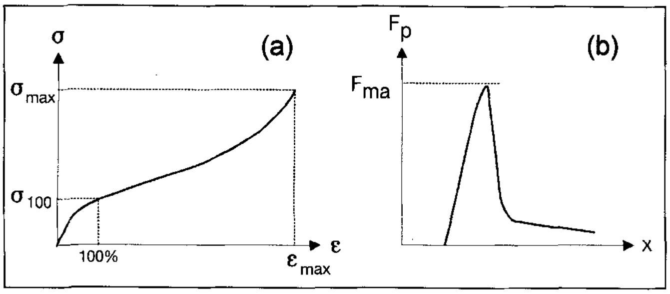

Figure 2: Stress-strain diagram of a tensile test (a) and force-distance diagram of a buckling test (b), both schematic.

Materials and Methods

The basic product of the Erlanger silver catheter is TPU "Tecothane" (Thermedics Inc.). Tecothane is a medical-grade polyurethane. Having passed USP Class VI, it is licensed for long-term usage. The product has been well tested in clinical practice at various grades of hardness (durometers) that range from 75 Shore A (very soft) to 75 Shore D (very hard). TPU with shore durometers between 85 A and 55 D are the most useful in catheters. To manufacture catheters with antimicrobial activity, 0.5 to 1.0 weight% of very finely dispersed silver particles are incorporated into Tecothane polyurethanes of different durometers. The incorporation is done in the molten state of the polymer. The characterization is mainly on the basis of the mechanical properties of the material and the buckling stability of the catheters manufactured from it.

Mechanical properties: The mechanical characteristics are obtained from a stress-strain diagram. The investigation was done on strands with diameters between 2 and 3 mm, produced by extrusion through a circular die. Strands with a length of 100 mm were fixed in the two clamping jaws of a tensile testing machine in such a way that the free clamping length l_0 between the jaws was 75 mm. The strand was then stretched with a testing speed of 200 mm/min in accordance with DIN 53504. The force F required was recorded as a function of sample elongation Δl until the strand was torn. The recorded force was converted to a stress $\sigma = F/A_0$, where A_0 was the initial cross section of the strand, and the elongation to a strain $\epsilon = \Delta l/l_0$. A stress-strain diagram was obtained as shown schematically in Figure 2 (a). The steep slope at the beginning, the subsequent flattening of the curve, the continuous increase in the slope until the sample tears, and the ultimate strain of several 100% are all characteristics of an elastomer. The stiffness of polyurethane elastomers is characterized by the stress at 100% strain, denoted here by σ_{100}. Strength and ductility of the material are characterized by the tensile strength σ_{max} and the ultimate strain ϵ_{max}, respectively. Figure 2 (a) shows how these characteristic parameters are obtained from the stress-strain diagram.

Buckling stability: Before a polyurethane type is selected, it has to be tested to establish whether catheters made of it with different geometries meet the requirements of practical use. One essential requirement of a cross-sectional profile is the buckling stability of the catheter.

Measurements of buckling strength are performed on sections of the catheter tube that are 10 mm in length. The pieces are placed between two plane-parallel plates in the tensile testing machine. The plates move together in the axial direction of the tube with a testing speed of 50 mm/min. The tube is compressed and finally buckles. Simultaneously the force of pressure F_p is recorded as a function of x, the distance covered. A schematic force-distance curve is shown in Figure 2 (b). Before the sample buckles, the force reaches a maximum value, F_{max}, the buckling force. The buckling force is the quantity that characterizes the buckling stability of the catheter.

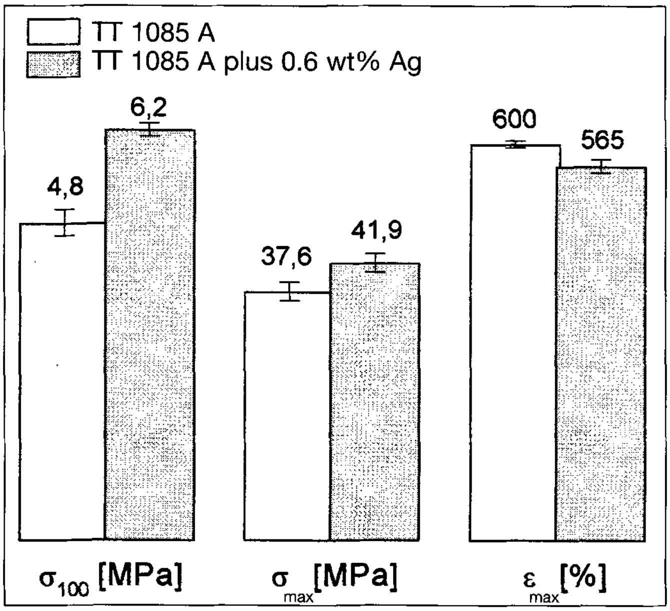

Figure 3: Stress at 100% strain, σ_{100}, tensile strength, σ_{max} and ultimate strain, ϵ_{max}, of Tecothane 1085 A with and without silver.

Results

Mechanical Properties

Samples made of pure Tecothane 1085 A (85 Shore A) were compared with samples made of the material containing silver as produced for the Erlanger silver catheter. The purpose of this investigation was to establish whether the incorporation of silver particles into the polymer caused any degradation in the properties of the material. As shown in Figure 3, the incorporation of silver has little effect on the mechanical properties of the material. The stress at 100% strain increased by approximately 25% and the tensile strength by about 10% when compared with the basic product. The ultimate strain of the product containing silver decreased by 5%.

In a further step two products containing silver with 85 Shore A and 95 Shore A, denoted here by TPU 1 and TPU 2, were blended in the molten state by means of extrusion to obtain intermediate durometers. The results of mechanical testing of the blends are presented in Figure 4. The stiffness of the blends (σ_{100}) varied linearly with the ratio of mixture to a good approximation. The strength (σ_{max}) was only affected to a minor extent.

Buckling Stability

The buckling stability of catheters with different cross-sectional profiles was investigated. Figure 5 shows the

results of buckling force measurements on catheters of identical TPU as a function of the cross section A. A ratio of wall thickness to outer radius that was similar for all samples was chosen.
It is clear that the buckling force increases overproportionally to the increasing cross-sectional area. To a good approximation the increase is parabolic (dashed curve), that is, twice the cross-sectional area yields a fourfold buckling stability.

Discussion

Mechanical Properties

The incorporation of silver particles does not affect the good mechanical properties of the thermoplastic polyurethane elastomer. The increase of stiffness and tensile strength (see Figure 3) can be due to molecular orientation and resulting hardening of the polymer during extrusion. It is less likely that the silver particles enhance stiffness and tensile strength significantly because their concentration in the polymer, 0.6% by weight (corresponding to 0.06% by volume), is extremely low. Since the TPU employed here has been extensively tested in catheter applications without silver, the product containing silver can also be regarded as suitable from the mechanical point of view.

Buckling Stability

The dependence of the buckling force on cross-sectional area, as shown experimentally, is in agreement with established theories on the buckling stability of material components. The buckling force F_{max} of bar-shaped components with constant cross section is given by Euler's formula,

$$F_{max} = \pi^2 E I_A / s^2$$

where E is the elastic modulus of the material, I_A the moment of inertia, and s the effective column length. For

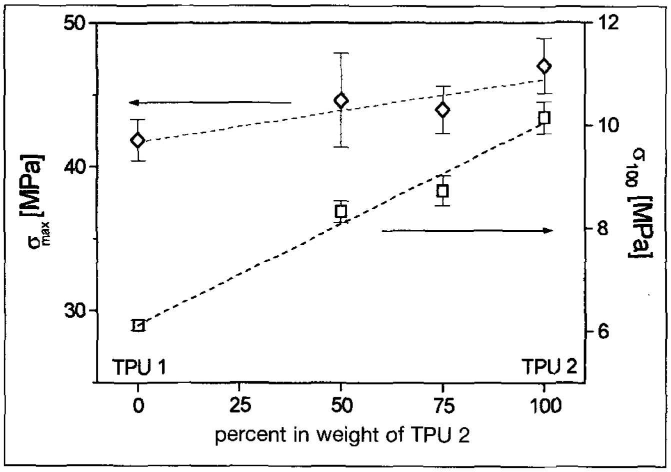

Figure 4: Stress at 100% strain σ_{100} and tensile strength, σ_{max}, as a function of the ratio of mixture of TPU1 (soft) and TPU 2 (hard). The dashed lines are linear regressions.

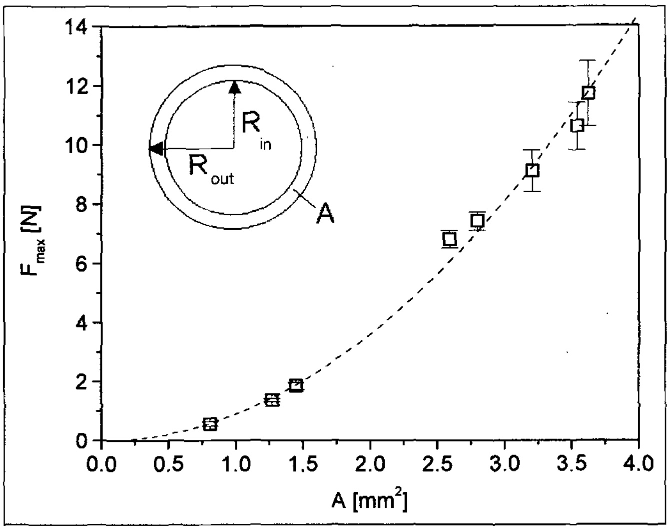

Figure 5: Buckling force, measured on single-lumen catheters, as a function of the cross-sectional area. The dashed curve is a parabolic fit. The ring is a schematic picture of the profile section of a single-lumen catheter, where A is the cross section; R_{in} and R_{out} are the inner and outer radii.

tubular components such as single-lumen catheters, the moment of inertia is calculated according to $I_A = \frac{\pi}{4}(R_{out}^4 - R_{in}^4)$ where R_{out} and R_{in} are the outer and inner radii of the catheter as indicated in Figure 5. For thin-walled catheters one can define $R = \frac{1}{2}(R_{out} + R_{in})$ and obtains the approximation $R_{out}^2 + R_{in}^2 \approx 2R^2$. It follows that

$$I_A = \frac{\pi}{4}(R_{out}^2 - R_{in}^2)(R_{out}^2 + R_{in}^2) \approx \frac{1}{2} A \cdot R^2.$$

For catheters with a constant ratio of wall thickness to radius, it holds that $(R_{out} - R_{in}) \propto R$, thus $A \propto R^2$, $I_A \propto A^2$, and $F_{max} \propto A^2$. The experimental data presented in Figure 5 show precisely this relationship. Thus the buckling force can be calculated for arbitrary profile sections with the help of Euler's formula if the elastic modulus E is a given material parameter. The calculation of the moment of inertia for multi-lumen catheters becomes more complex and may be facilitated by electronic image processing.

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