MATERIAL SIMULATION OF POLYMERS CONTAINING SPHERICAL STRUCTURES

Achim Frick[1], Melissa Matzen[2], Timo Dolde[3]

[1,3]*Aalen University, Inst. Polymer Science and Processing iPSP, Aalen (Germany),*
[2]*University of Bremen, Bremen (Germany);*
Email: Achim.Frick@htw-aalen.de

Abstract: One of the keys for successful polymer product development is proper material selection. It is recommended to apply tailor sized polymers in order to realize best product performance with respect to the requirements. Material simulation is a possibility to predict material data from modified polymers, e.g. particle filled polymer, for strength calculation purpose, which is eminent part of the product design process. A method to simulate stress-strain behaviour of polymers containing spherical structures is shown for TPU material.

Keywords: *Polymer, Morphology, Material Simulation, Computer Aided Product Development*

1. General Introduction

A successful polymer product requires a proper material selection. Therefore it is necessary to integrate both a material based strength calculation and structural optimization as the two main elements of a computer aided product developing process, **Figure 1**. Material simulation is a possible tool to provide material data from any polymer modification for strength calculation.

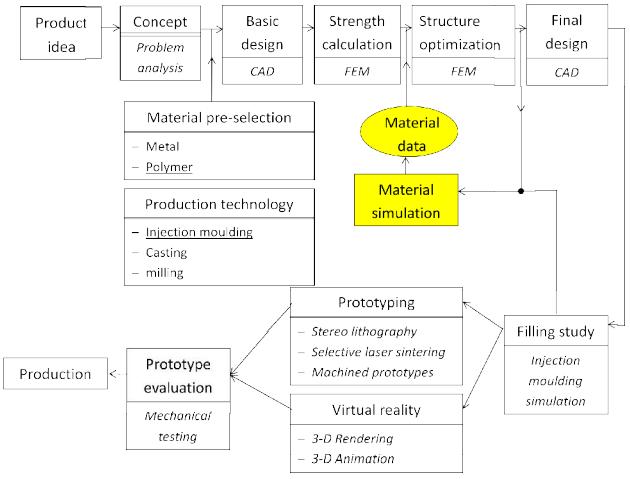

Figure 1: *Product development process from the idea to the final production*

Material properties of thermoplastic polymers depend on the one hand on their thermal history, due to the processing conditions during moulding, as well as on a possible tailor sizing by adding e.g. fillers or reinforcement to the polymer matrix.

To study the possible consequences of such variations for the strength behaviour of the polymer a material simulation is recommended. It provides a fast and helpful method for advanced product development.

2 Investigated Material

Segmented thermoplastic polyurethanes TPU belong to the class of TPE and they show soft and rubberlike behaviour at RT. Nevertheless they perform comparably strong, are oil resistant and behave superior abrasion resistant, which recommend them for e.g. sealing applications. But the properties of TPU are highly influenced by their morphology developed during the melt processing and subsequent solidification process. The stress-strain behaviour of TPU is observed to be strongly dependent on the present crystalline domain structure, which shows to be spherical shaped. Also for semi crystalline polymers the spherical crystalline fraction determines the end use properties of the material. Concerning that a material simulation can provide to better material understanding basically and can also suggest optimal morphological structure for the polymeric material in order to perform best in application.Thermoplastics can further contain fillers such as glass balls or minerals particles to enhance the strength and stiffness of the basic

material. Material simulation gives a possibility to predict the material behaviour of modified polymers for strength calculation purpose. It can provide information for improved material selection and qualification for a demanded product under development.

Material simulation requires material parameters for input in order to model a polymeric material as a part of product development process. There are two possibilities to obtain the parameters. Either a theoretical based material system can be generated or the material data are received by analyzing a real polymer sample.

3 Modelling

3.1 GENERATED STRUCTURE

To study theoretically on a possible influence of spherical inclusions in a polymeric material matrix a determined distribution of the spheres with a chosen radius, **Figure 2**, is input into the software, e.g. Digimat® from Xstream-Engineering, and a representative volume element (RVE) is generated. The software then provides the stress-strain curve of modeled material. It is a way to simulate material behavior depending on its spherical inclusion fraction and inclusion size and distribution, where the inclusions may represent spherulitical crystalline structure in semi crystalline polymers or any filler with an aspect ratio near 1.

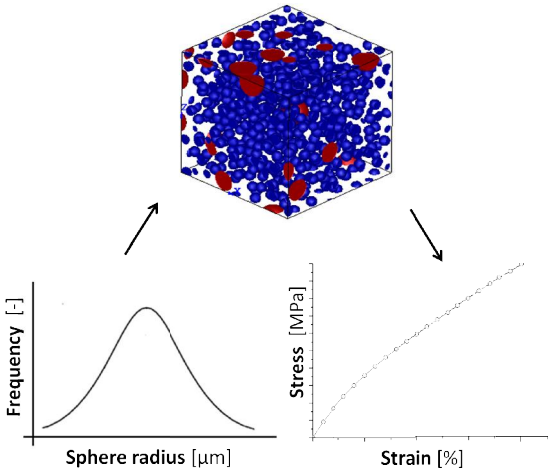

Figure 2: *Virtual material simulation based on generated structure*

A virtual section view of this RVE can be taken to visualize and study the morphology and it also can be compared with a micrograph taken from a real cross section of a material sample micro structure, in order to validate how realistic the modeled morphology is.

3.2 DERIVED STRUCTURE

To approach on the evidence of a certain morphological structure on the mechanical behavior of a polymeric material sample it is helpful to model this real existing material morphology by means of material simulation in a reverse procedure.

As a starting point a light microscopy (LM) or even transmission electron beam microscopy (TEM) micrograph is observed and the distribution of the detected spherical inclusions, e.g. spherulits, is identified, see **Figure 3**.

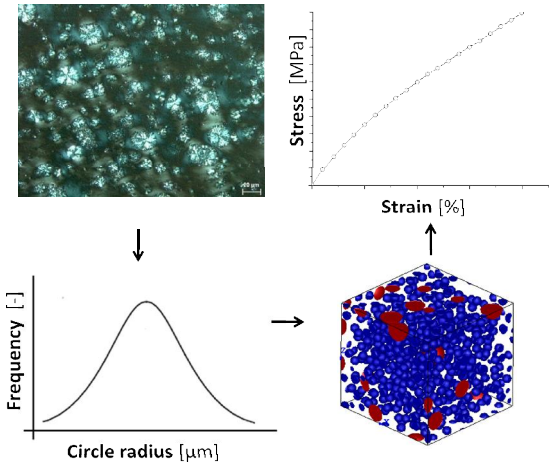

Figure 3: *Real material modelling based on the derived structure*

Using these information received a RVE is generate and is basis for further material simulation procedure, in order to establish the stress-strain behaviour of the modelled material structure.

The challenge hereby is on one hand to analyse properly the inspected morphological structure in the 2D micrograph and on the other hand to reconstruct the size and dispersion of the observed inclusions in the regarded volume.

3.2.1 Image analysis of micrographs

A computer assisted image analysis of morphological micrographs seems problematic regarding a proper detection and reproducible results.

As a basic requirement for computer assisted determining the diameter of a spherical structure embedded in a grey environment it needs to have a sufficient contrast between the both structures next each other. The grey values of each of them must differ strongly in their brightness. Otherwise an automatic detection is not possible, whether due to insufficient contrast of the structure intended to get measured or due to random variation of the

structure in geometry and deviation from the predefined geometry.

If an automatic evaluation of the micrograph of a material morphology is not feasible and the inspection is done visually then there is no necessity for any contrast optimization and correction of inhomogeneous grey values distribution in the image due to the varying section thicknesses of the previous inspected microtome section under transmission light microscope. To avoid inconsistencies in the measuring results by visual evaluation of morphologies it is recommend involving always the same person for inspection task.

3.2.2 Relation between measured circle radius and the radius of the sphere

When observing on a cross section of a material filled with spherical inclusions randomly dispersed, and even all the inclusions have same diameter, the circle shaped cross sectional areas of those inclusions show different diameters.

The mathematical calculation of the diameter distribution of spherical inclusions in a matrix material from the estimated radius distribution of the measured circle shaped areas is mathematically an ill-defined problem [3], which needs to be solved. It is quite ambitious and requires expressed mathematical skills. It is like "tomato salad problem" and to estimate the diameter of a tomato by measuring the diameter of its slices. Due to the difficulties to solve this mentioned problem some approximation methods have been suggested. Wicksell [4] was the first who described in 1925 in a treatise titled "corpuscle problem" the relation between a measured radius of an arbitrary section of a sphere and its real radius. Bach [5] adopted in 1958 the problem and gave refined solution regarding the size distribution of inspected spherical sections in translucent slices of finite thickness.

The approach of Bach [5] uses the second Volterra integral to describe the relationship between the size distribution of spherical radius and circle radius, see equation 1,

$$g\left(\mathrm{R}^{\mathrm{Circle}}\right) = 2 \cdot F \cdot \mathrm{R}^{\mathrm{Circle}} \cdot d\mathrm{R}^{\mathrm{Circle}} \cdot \int_{\mathrm{R}^{\mathrm{Circle}}}^{\infty} \frac{G\left(\mathrm{R}^{\mathrm{Sphere}}\right) d\mathrm{R}^{\mathrm{Sphere}}}{\sqrt{\mathrm{R}^{\mathrm{Sphere}^2} - \mathrm{R}^{\mathrm{Circle}^2}}} + \delta \cdot G\left(\mathrm{R}^{\mathrm{Circle}}\right) \quad (1)$$

It means:

$G\left(\mathrm{R}^{\mathrm{Sphere}}\right)$	Sphere radius distribution
$g\left(\mathrm{R}^{\mathrm{Circle}}\right)$	Circle radius distribution
F	Cross section area
$\mathrm{R}^{\mathrm{Sphere}}$	Sphere radius
$\mathrm{R}^{\mathrm{Circle}}$	Circle radius
δ	Sample thickness

The calculation method according to Fullman [6] is simple compared to the suggested method of Bach. Fullman assumed that the sphere radius is identical to the average radius of Gaussian distributed circle radii, **Figure 4**, which are detect.

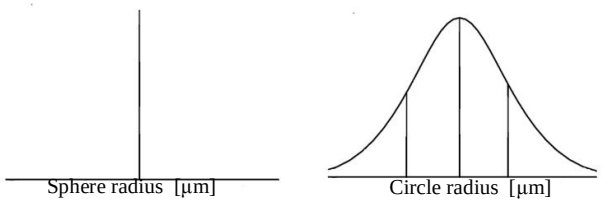

Figure 4: *left: the sphere size distribution (distinct); right: detected cross section radius distribution*

According to that assumption, Fullman concluded the sphere radius $\boldsymbol{R^{sphere}}$ to be equal the circle radius $\boldsymbol{R^{circle}}$.

$$R^{circle} \approx R^{sphere} \quad (2)$$

Mathematically, the Bach method is relatively elaborative, but it provides excellent results. The solution of Fullman, which bases on the simplest approach to determine the relationship between the radius of a two dimensional circular section and the three dimensional sphere radius, provides at minor calculation effort also useable results.

3.2.3 Relation between measured cross sectional area and the volume

To simulate a filled material it is essential to know on its composition (filler volume fraction) as well as on the inclusion size and distribution. So the content volume of filler has to be estimated from a micrograph of the morphological structure of a sample, **Figure 5**. It is necessary to estimate the 3D volume of an inclusion from the diameter of its two-dimensional (2D) cross sections. **Figure** 5 depicts the problem.

According to [7] the sum of circular areas $\sum_{i=1}^{n} F_i$ is equivalent to the total volume of the spheres $\sum_{i=1}^{n} V_i$. Thus the following equation 3 expressing the relationship between the area fraction and volume fraction is valid.

$$\frac{\sum_{i=1}^{n} F_i}{F} = \frac{\sum_{i=1}^{n} V_i}{V} \qquad (3)$$

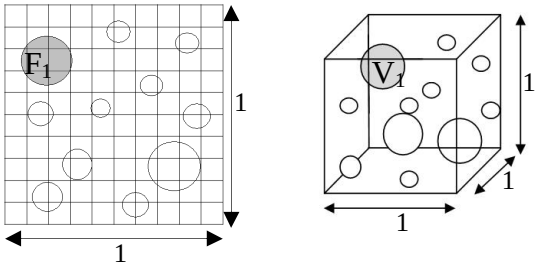

Figure 5: *Left: micrograph of the cross sectional area of samples with inclusions; right: reconstructed volume (F_1: circular area, V_1: sphere volume)*

By means of image analysis the cross section of a material containing spherical inclusions both, the sphere radius distribution of the inclusions, as well as the volume fraction of the spheres, can be estimated.

4. TPU Material Modelling

Material modelling requires first a mathematical equation which is adapting to the specific material deformation behaviour and thus fits to its stress-strain behaviour best. For instance Mooney-Rivlin equation can be used for modelling elastomeric materials such as TPU. The mathematical concept behind this model is a hyper elastic approach.

In case of segmented thermoplastic polyurethanes TPU the macromolecular chains exist from sequentially linked hard and soft segments. The hard segments can build rigid domains in the soft segment matrix, depending on a possible phase separation between both, which is ruled by the melt processing conditions during moulding. If the material will be processed at high melt temperature the hard segments does not segregate and shape distinct domains, the TPU therefore shows almost transparent. In such case there is no expressed crystalline super structure in the transmission light micrograph visible. The material is considered to be amorphous in its morphological structure.

Figure 6 shows a measured stress-strain curve of an amorphous TPU sample (nominally 94 Shore A durometer hardness) processed at a melt temperature of 250˚C and its best fit curve considering Mooney-Rivlin equation. The material model describes the measured data quite well, especially at higher strain more than 40%.

Based on the fit curve, considered as the material model representing the amorphous matrix material, it is now possible to study the consequences of a certain crystalline volume fraction in the amorphous matrix on the mechanical properties of the considered TPU by simulation. The material simulation of partially crystalline TPU has to approach the stress-strain behaviour of a RVE containing an amount of hard and spherical shaped inclusions, which represents the crystalline structure.

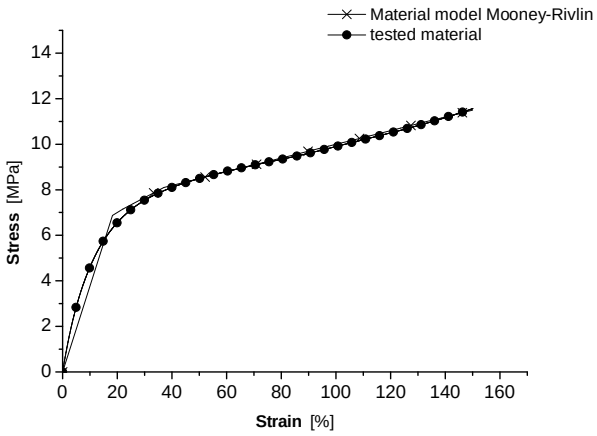

Figure 6: *Modelling stress-strain behaviour of amorphous TPU by Mooney-Rivlin approach (fit curve calculated with software ABAQUS 6.7)*

The further simulation of partially crystalline material requires the mechanical properties, e.g. the Young's modulus of the pure hard segments of TPU. Unfortunately the mechanical properties of the pure hard segments or even of the hard domains cannot be determined easily because it is almost impossible to approach those separately and simply. Therefore it needs to find approximate material data for crystalline structure.

It is well known that a homo-polymeric polyoxymethylene (POM-H) represents a strongly crystalline polymer and has crystalline content up to 90% [8, 9, 10]. Thus in a first order approach the TPU hard segments are considered to have a similar stiffness than POM-H. The Young´s modulus is taken to be 3000 MPa for the hard segments.

4.1. SIMULATION OF CRYSTALLINE CONTENT

In order to simulate the influence of hard segment domains in amorphous TPU material representative volume elements (RVEs) of TPU were generated containing spherical shaped

crystalline fraction content. The RVE generation procedure was as described before and RVE created using Digimat software. The diameter was considered 10 μm for simulating crystalline structure when the volume fraction content varies from 0 to 30 vol%.

Figure 7 shows the influence of growing content of crystalline structure on the stress-strain behaviour of TPU, the material becomes significantly stiffer and its strength rises. It becomes obvious that the TPU must perform in service application quite different depending on its present crystalline domain fraction. The stress-strain behaviour of this material depends hardly on the melt processing conditions during manufacturing process.

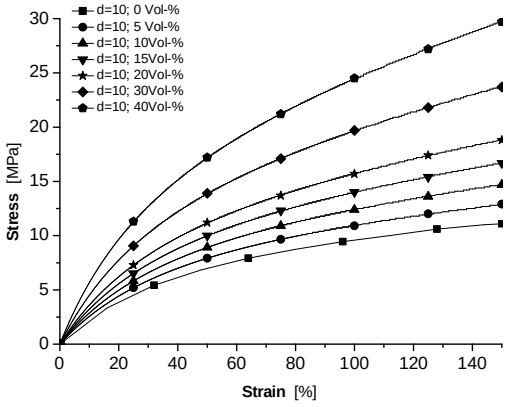

Figure 7: *Simulated stress-strain curves for TPU with different vol.% crystalline domain content (d: sphere diameter of inclusion)*

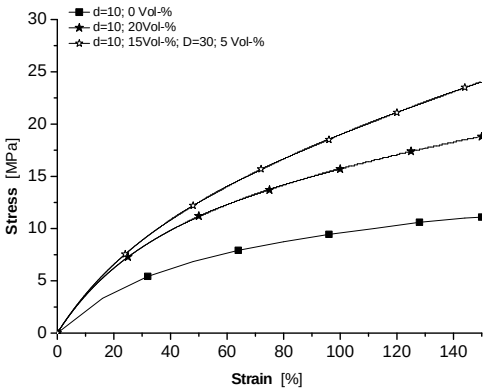

Figure 8: *Simulated stress-strain curves for TPU, amorphous state and with 20 vol.% crystalline domain content (mono and bi-sized inclusions, d: sphere diameter of inclusion 1, D: sphere diameter of inclusion 2)*

Assuming the crystalline domain fraction in total to be 20 vol% and it exists from 2 different diameter sized inclusions (10 μm and 30 μm) it is calculate by simulation, that the bi-modal crystallinity gains better material strength behaviour than a mono-modal one, **Figure 7**

5. Summary

Material simulations allow to model polymeric material with incorporated inclusions, such as crystalline domains or fillers, in order to study the resulting mechanical behaviour. The data received can be used for within the product development process and also for material science purposes.

The simulation possibility was approached on segmented TPU material.

References

[1] A. Frick, M. Mikoszek: Predispositions to failure of Polyurethane Sealings: Relation between Morphology and Visco-elastic Properties, p. 413-414, full paper: S1205_A0273 in Gomes, J.F.S.; Meguid, S.A. (editors): Integrity, Reliability and Failure: challenges and Opportunities, Edition INEGI, 2009 (ISBN 978-972-8826-22-2)

[2] A. Frick, M. Mikoszek, M. Kaiser: Qualität von TPU-Dichtungen: Über den Einfluss der Morphologie auf die Gebrauchseigenschaften in Dichtungstechnik Jahrbuch 2010, S. 356-372

[3] A. Louis: Inverse und schlecht gestellte Probleme; Stuttgart; Teubner Verlag; 1989.

[4] S. Wicksell: The corpuscle problem, A mathematical study of a biometric problem; Biometrika; 1925, A-17; S. 84–99

[5] G. Bach: Über die Größenverteilung von Kugelschnitten in durchsichtigen Schnitten endlicher Dicke; Diss; Universität Gießen; 1959; S. 2ff.

[6] R. Fullman: Measurement of approximately cylindrical Particles in Opaque Samples; Transactions AIME;1953; A-197; S. 1267ff.

[7] W.Rostoker, J.Dvorak: Interpreatation of metallographic structures; Academic Press Inc.; 1965; S. 198.

[8] G. Becker, L. Bottenbruch, D. Braun: Technische Thermoplaste: Polycarbonate, Polyacetate, Polyester, Celluloseester; München; Hanser Verlag; 1992; S. 333.

[9] [Online] Wapedia: 5.07.2010; http://wapedia.mobi/de/Kristallisation_(Polymer).

[10] G. Ehrenstein, G. Riedel, P. Trawiel: Praxis der thermischen Analyse von Kunststoffen; München; Hanser Verlag; 2003; S. 74.