Influence of Crystallization and Filler Degrees on Viscoelastic Properties of Rubber Compounds

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Overview

The dimensioning of injection heads for the extrusion of rubber profiles is exclusively based on empiric knowledge of the non-linear material flow behavior. Till now, the geometry of the appropriate profile is achieved by empiric adaptation of the extrusion die. This was one of the motivations for a research project concerning the visco-elastic material behavior of rubber compounds. These are used for window sealings, pipeline constructions, bridge dilatations and various parts of cars.

The investigations were performed with various rubber compounds used in industry, with amorphous and crystalline structured EPDM as basis polymer and mainly carbon black and chalk as filler with different filler degrees. To investigate the viscoelastic behavior experiments with a capillary-viscometer and a rubber process analyzer were performed. In addition to the extrusion pressure the die swell has been determined for all capillary-experiments after the exit of the capillary.

The investigations cover the discussion of three viscoelastic properties, the shear strain rate dependent viscosity function [1], the die swell phenomenon [2] and the dynamic moduli, i.e. storage and loss modulus [3].

Literature:

[1] H.W. Müllner, J. Eberhardsteiner, P. Mackenzie-Helnwein: Constitutive Characterization of Rubber Blends by Means of Capillary-Viscometry, Journal of Non-Newtonian Fluid Mechanics, 141 (2007): submitted.
[2] H.W. Müllner, J. Eberhardsteiner, W. Fidi: Rheological Characterization of the Die Swell Phenomenon of Rubber Compounds, Polymer Testing, 26 (2007): submitted.
[3] H.W. Müllner, A. Jäger, E.A. Aigner, J. Eberhardsteiner: Experimental Identification of Viscoelastic Properties of Rubber Compounds by Means of Torsional Rheometry, Meccanica, 42 (2007): submitted.

Die Swell - Swell Value Measuring Unit

For this investigation six rubber compounds were investigated, two different chemical conditions of EPDM, amorphous and crystalline, with three different filler degrees each (see Table).

compound code		EPDM A	EPDM B	EPDM C	EPDM D	EPDM E	EPDM F
molecular structure	[ ]	amorph.	crystal.	amorph.	crystal.	amorph.	crystal.
$ML(1+4)$	[ME]	59.9	64.3	63.7	62.4	66.3	64.3
Shore-grade	[ShA]	67.0	78.0	64.0	76.0	59.0	72.0
density	[g/cm^3]	1.294	1.298	1.209	1.214	1.098	1.104
filler degree	[phr]	high	high	average	average	low	low

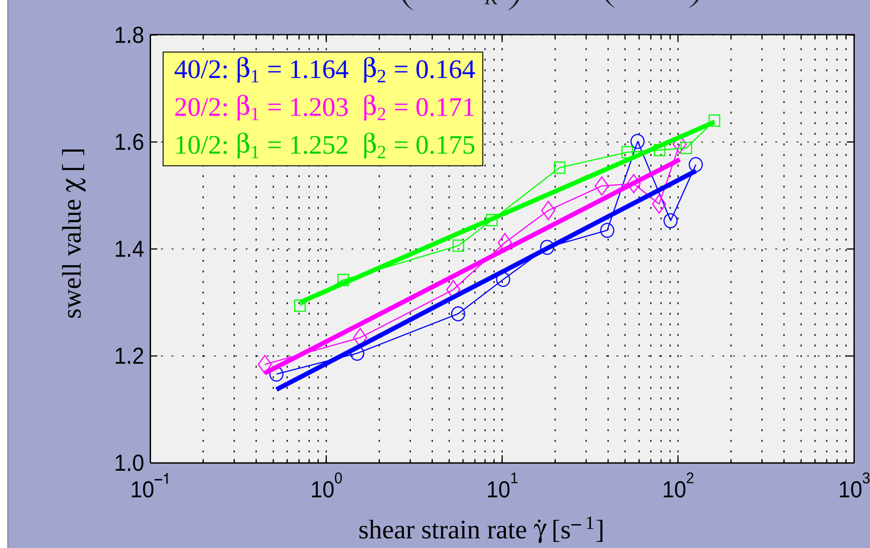
Elastic Deformation - Material Parameter describing Die Swell

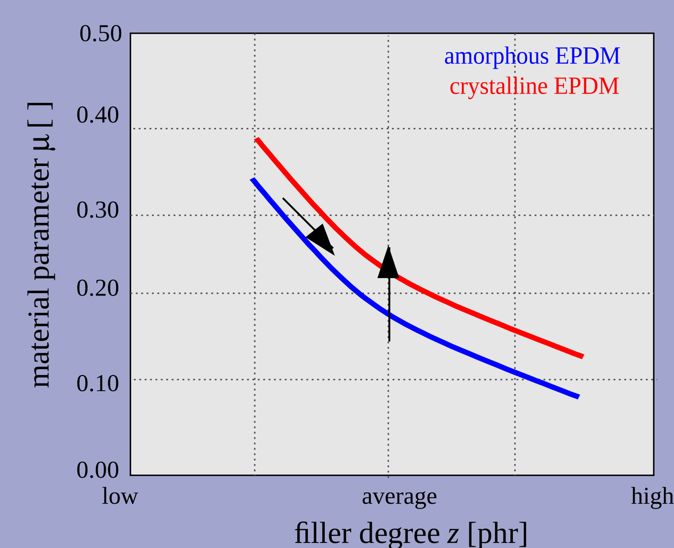
$$\chi_{calc} = \left(\frac{d}{D}\right)^2 = \beta_1 + \beta_2 \lg\dot{\gamma}$$

$$\beta_1 = \beta_1(L,D,T,\mu) = \left(1+\frac{D}{L}\right)^{\mu}\left(1+\frac{\bar{D}}{D}\right)^{\mu}\left(1+\frac{\bar{T}}{T}\right)^{1-4\mu}$$

$$\beta_2 = \beta_2(D,T,\mu) = \left(1+\frac{D}{D_K}\right)^{1+\frac{0.075}{\mu}}\left(1+\frac{\bar{T}}{T}\right)^{1-4\mu}$$

χ ... swell value
D ... diameter of capillary die
L ... length of capillary die
T ... melt temperature
μ ... material parameter

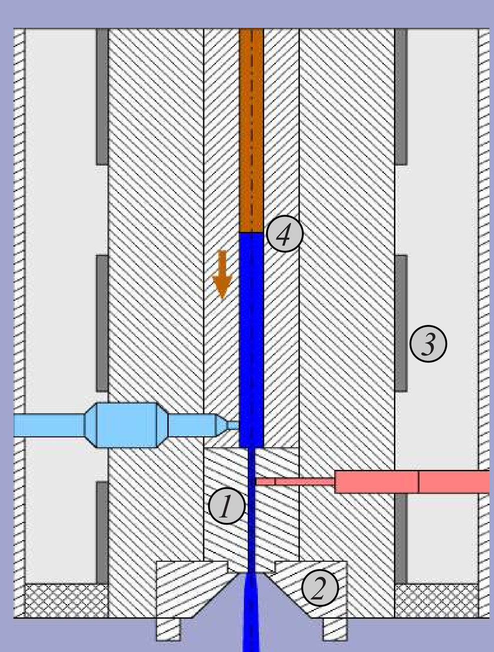




The parameter of a capillary experiment, length and diameter of the used capillary, the melt temperature, and the corresponding shear strain rate, have a certain influence on the die swell of non-Newtonian fluids. With an empiric relationship these influences on the die swell phenomenon are investigated. The equation allows characterization of die swell by means of only one material parameter [2].

Furthermore, the influence of variation of the crystallization and filler degree of the compounds on the die swell is covered by only one parameter, too. This parameter is always higher for rubber compounds consisting of polymers with crystalline structure. For different filler degrees, a decrease of die swell with increasing filler content is detected.

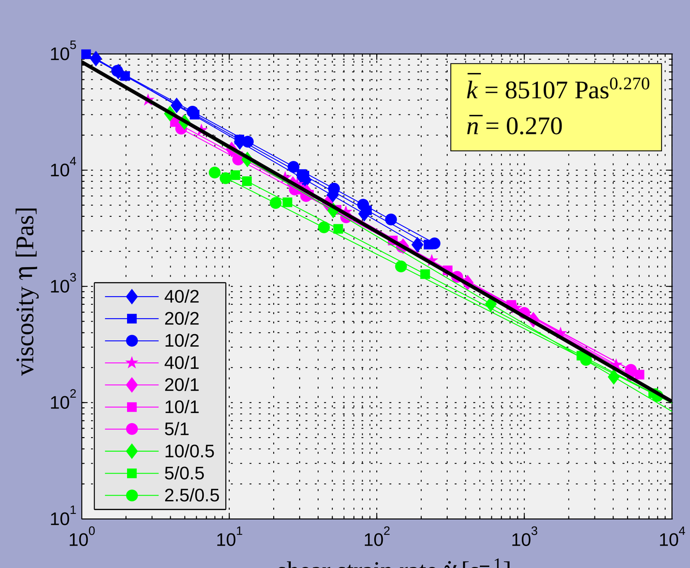
Dynamic Viscosity - Capillary Viscometry



testing melt
test stamp
pressure sensor
temperature sensor

(1) capillary
(2) capillary nut
(3) radiator
(4) testing chamber

Shear-Thinning Flow Behavior - Power Law

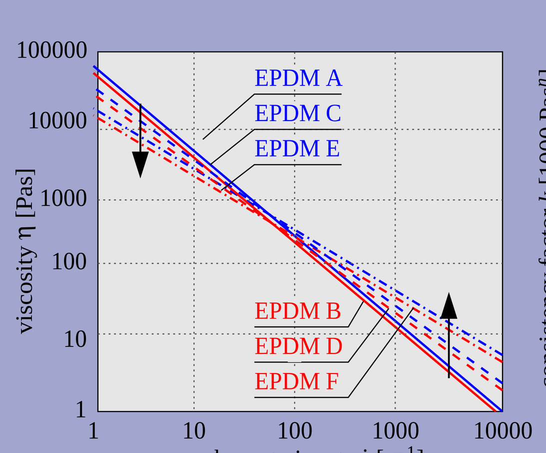


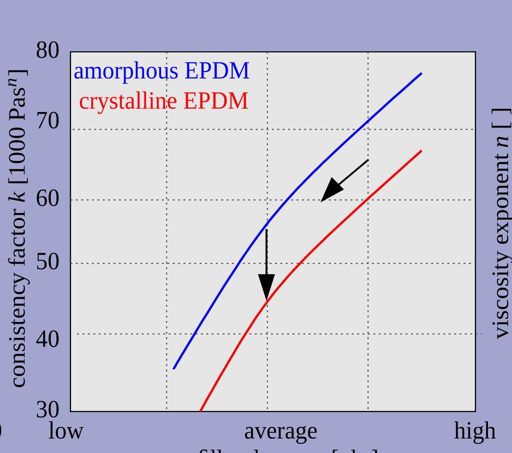
$$\tau(\dot{\gamma}) = \eta(\dot{\gamma})\,\dot{\gamma} \quad \text{with} \quad \eta(\dot{\gamma}) = k\,\dot{\gamma}^{\,n-1}$$

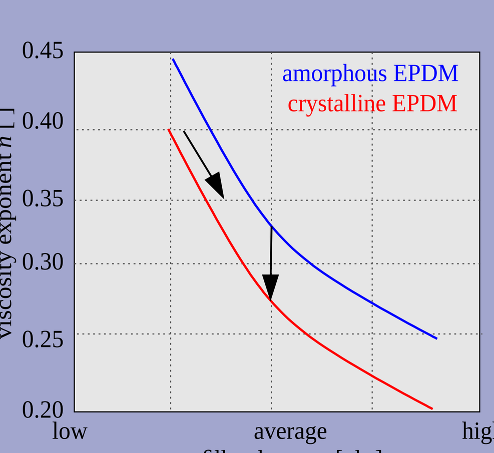
η ... dynamic viscosity
$\dot{\gamma}$ ... shear strain rate
k ... consistency factor
n ... viscosity exponent

Rubber blends are shear-thinning. In order to determine the viscosity of rubber experiments with a capillary-viscometer are required. The transformation of the experimental results into a viscosity-shear strain rate correlation is done by means of a material characterization by Müllner et al. [1]. For the description of this nonlinear correlation a power law is used, introducing two constants.

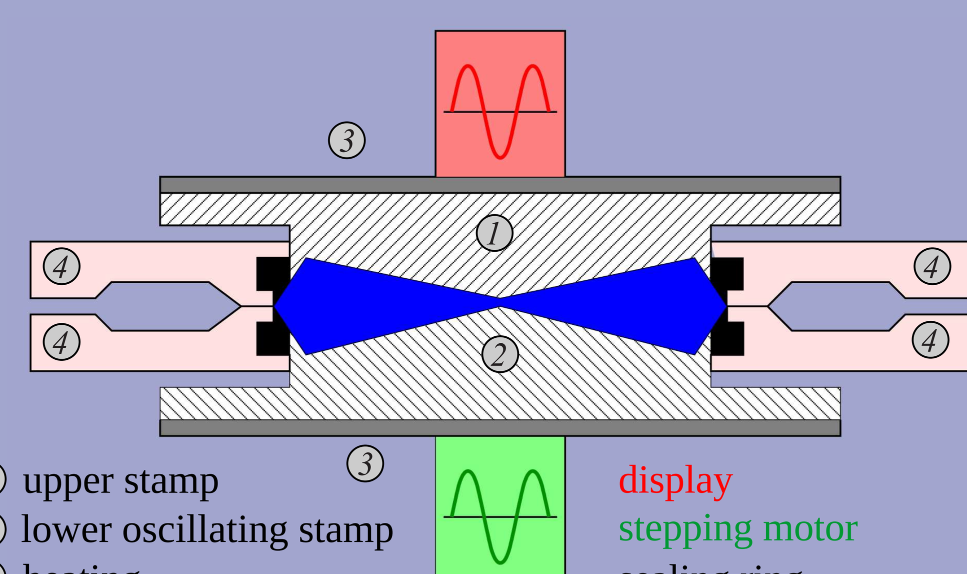
The application of the power law allows identification of the influence of both, the crystallization degree of the basic polymer and of the amount of used filler material, on the shear-thinning properties of the investigated rubber compounds. Using a double-logarithmic plot for the viscosity function, a clear trend for both properties is detected. Using EPDM with amorphous chemical structure, i.e. a low crystallization degree, leads to a decrease of the consistency factor.ler content of the rubber compound, i.e. an increase of the filler degree, yields a decrease of the viscosity exponent.







Elastic Moduli - Torsional Rheometry



(1) upper stamp
(2) lower oscillating stamp
(3) heating
(4) sealing

display
stepping motor
sealing ring
testing melt

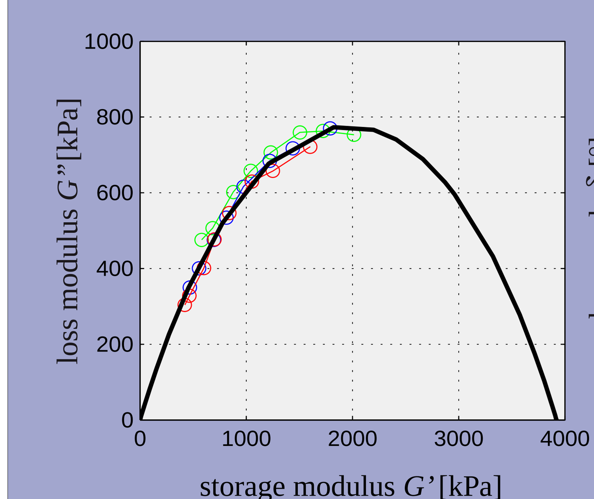
Viscoelastic Material Behavior - Huet model

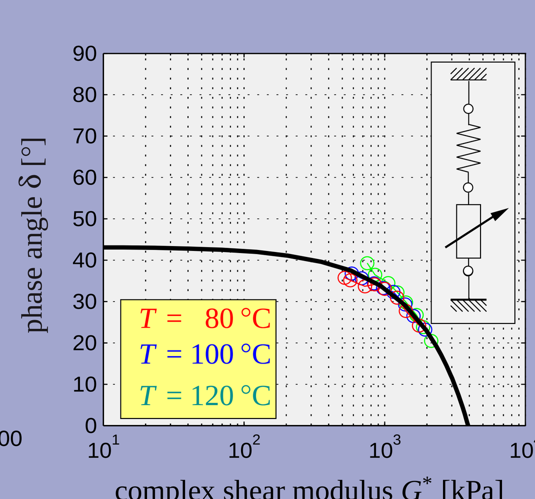
$$G'(J_0,J_1,m_1) = \frac{J_0}{\Delta} + \frac{J_1}{\Delta}\Gamma(1+m_1)\omega^{-m_1}\cos\frac{m_1\pi}{2}$$

$$G''(J_0,J_1,m_1) = \frac{J_1}{\Delta}\Gamma(1+m_1)\omega^{-m_1}\sin\frac{m_1\pi}{2}$$

$$\text{with } \Delta = J_0^{\,2} + 2J_0J_1\Gamma(1+m_1)\omega^{-m_1}\cos\frac{m_1\pi}{2} + \left(J_1\Gamma(1+m_1)\omega^{-m_1}\right)^2$$

$J_0 = J_1$ ... creep compliance
m_1 ... exponent for nonlinear dashpot
G' ... storage modulus
G'' ... loss modulus





For the experimental investigation of rubber compounds by torsional rheometry, the simplified Huet model reproduces the viscoelastic behavior satisfactory [3].

Under consideration of two material parameters, a clear trend for both properties is detected. Using EPDM with an amorphous chemical structure leads to an increase of the viscous properties of the corresponding rubber compound, i.e. to an increase of the phase angle. Furthermore, an increase of the filler content of the rubber compound yields an increase of the viscous properties, i.e. an increase of both the loss modulus and the phase angle, respectively.