

Polymere Netzwerke: Struktur, Theorie und Anwendung



**Prof. Dr. Jens-Uwe
Sommer**
Tel.: 0351 4658-750
sommer@ipfdd.de



Prof. Dr. Gert Heinrich
Tel.: 0351 4658-360
gheinrich@ipfdd.de

Durch die Vernetzung von Polymeren werden Flüssigkeitseigenschaften (Viskosität) mit Festkörpereigenschaften (Formbeständigkeit, Lösungsmittelbeständigkeit) kombiniert. Eine neue Klasse von Netzwerken, welche nur durch die Verhakung von Ringpolymeren entsteht, ermöglicht die genauere Untersuchung der Rolle der Topologie auf die thermodynamischen Eigenschaften, insbesondere die Quellung von Netzwerken. Solche „Olympischen Gele“ zeigen in der Simulation eine Abnahme des Quellgrades mit zunehmender Kettenlänge. Dieses überraschende Ergebnis kann durch die Rolle der nicht-affinen Deformation erklärt werden, welche durch die unvollständige Verhakung der sich räumlich durchdringende Ringe entsteht (Phys. Rev. Lett. 112, 238001 (2014)). Diese Arbeiten liefern auch einen neuen Zugang zum Verständnis der Rolle der Topologie für chemisch vernetzte Gele. Stimuli-responsive Polymernetzwerke stellen eine Klasse von funktionalen Materialien dar, deren elastische Eigenschaften durch Licht oder äußere Magnetfelder kontrolliert werden können. Theoretische Untersuchungen zeigen die Rolle der Verteilung und der Probengeometrie auf die magneto-elastischen Kopplungseigenschaften (Soft Matter 10, 2213 (2014)). Vernetzte Polymere zeigen dynamische Eigenschaften über einen sehr großen Zeitbereich, die nicht durch einen einzigen universellen Prozess beschrieben werden können. Durch einen Multiskalen-Ansatz für die Spektraldichte der Relaxationszeiten, welcher verschiedene dynamische Prozesse in unterschiedlichen Zeitbereichen kombiniert, ist es gelungen das Verhalten des dynamischen Moduls für ungefüllte Polymernetzwerke über 14 Größenordnungen der Zeit zu beschreiben (Macromolecules 47, 4813 (2014)). Die Arbeiten im anwendungsorientierten Bereich des ST3 erfuhren eine Würdigung durch zwei Preise: Dr. Karsten Brüning wurde anlässlich der TireTechExpo 2014 in Köln mit dem Young Scientist Award ausgezeichnet, der das hohe Interesse der Reifenindustrie an seinen Ergebnissen zur Aufklärung der Kinetik der dehnungsinduzierten Kristallisation von Naturkautschuk widerspiegelt. Für seine Dissertation auf dem Gebiet der funktionalen Elastomer-Nanokomposite erhielt Dr. Sandip Roj den Förderpreis der Deutschen Kautschuk-Gesellschaft. Die experimentelle

Charakterisierung elastomerer Werkstoffe war Gegenstand des Work-Shops „Nicht-konventionelle Charakterisierung von Gummi“, der mit über 75 Teilnehmern vorwiegend aus der Industrie die hohe Anwendungsrelevanz diesbezüglicher Arbeiten im ST3 unterstreicht. Das Gebiet funktioneller Elastomer-Nanokomposite wurde durch eine Reihe von Publikationen weiter ausgebaut, z. B. “Evidence for an in situ developed polymer phase in ionic elastomers” (Macromolecules 74(2014) 3463), „The role of linked phospholipids in the rubber-filler-interaction in carbon nanotube filled natural rubber composites” (Polymer 55(2014) 4738) und “Unmodified LDH as reinforcing filler for XNBR and the development of flame-retardant elastomer composites” (Rubber Chem. Technol. 87(2014) 606).

Polymere Netzwerke: Struktur, Theorie und Anwendung

The swelling of olympic gels

Michael Lang, Jakob Fischer, Marco Werner, and Jens-Uwe Sommer

Olympic gels [1, 2] are networks made of cyclic polymers ("rings") connected by the mutual topological inclusion of polymer strands, see Fig. 1, with their elastic properties depending exclusively on the entanglements that are fixed by the linking of the rings.

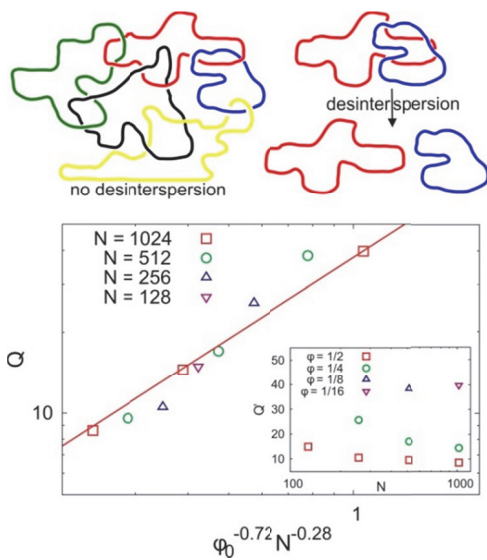


Fig. 1:
Top left: sketch of an Olympic gel. Top right: desinterspersion of non-concatenated strands. Bottom: The scaling of the equilibrium degree of swelling as function of the degree of polymerization, N , and the polymer volume fraction at preparation conditions, φ_0 . The line indicates a scaling according to $Q \propto N^{0.28} \varphi_0^{-0.72}$. Inset: unscaled data.

This particular difference to conventional polymer networks and gels makes these materials an interesting model system, since the pristine effect of entanglements on the thermodynamic properties of polymers is accessible. In particular, such gels could reveal the role of entanglements for the equilibrium swelling of polymer networks, which is an outstanding problem in polymer physics. Since the term Olympic gels has been coined by de Gennes [1], however, the challenge to synthesize such materials has not been mastered yet, although possible

pathways for their synthesis have been proposed [2,3].

Recently [4], we constructed Olympic gels by computer simulations in order to characterize their topological state and to simulate isotropic swelling in an a-thermal solvent. We found that the equilibrium degree of swelling, Q , of Olympic gels is described by a negative power as function of the degree of polymerization, N , of the rings, see Figure 1, in marked contrast to standard models of network swelling [5] that predict an increasing degree of swelling for larger N . We showed in Ref. [4] that this result is a direct consequence of a desinterspersion process originally proposed by Bastide [6], which allows polymer rings to swell in part at no elastic deformation.

The key to understand this unusual swelling behavior is the observation that the number of overlapping rings in the swollen state is approximately the same as the number of concatenations per ring. Thus, only concatenated rings remain in overlap at equilibrium swelling, while non-concatenated pairs of rings that were overlapping at preparation conditions desintersperse during swelling. Since the degree of concatenation and the number of overlapping rings depend on N and the polymer volume fraction at preparation conditions, φ_0 , swelling equilibrium of an Olympic gel could be expressed [4] by

$$Q \propto N^{-0.19} \varphi_0^{-0.75}, \quad (1)$$

with the same parameters but at a clearly different scaling as the text-book estimate [5] for a fully affine swelling of a conventional polymer network,

$$Q \propto N^{0.57} \varphi_0^{-0.25}. \quad (2)$$

The good agreement of our simulation data, that fits best to

$$Q \propto N^{-0.28} \varphi_0^{-0.72} \quad (3)$$

with equation (1) is a first indication, that our model describes the main features of the swelling of Olympic gels. A second, probably more striking result is that for Olympic gels, a larger equilibrium degree of swelling must be correlated with a larger non-affine contri-

Keywords
olympic gel
desinterspersion
non-affine swelling
Monte-Carlo simulation

Polymere Netzwerke: Struktur, Theorie und Anwendung

Keywords
in-situ synthesis
polyurethane-urea
nitrile butadiene rubber
self-compatibilization
structural/mechanical
characterization

tribution to swelling. This tendency was also confirmed by our simulation results. The results of our study [4] have enormous potential to revolutionize our understanding of the equilibrium degree of swelling of conventional polymer networks: for the first time it was possible to estimate the non-affine contribution to the equilibrium degree of swelling. Current investigations, therefore, focus on the transfer of these results to conventional networks in order to quantify non-affine contributions to swelling, which are known since decades [6], but still lack a theoretical description.

Sponsor:
 Deutsche Forschungsgemeinschaft,
 Projekt LA 2735/2-1

- [1] P. G. De Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, Ithaca (1979).
- [2] E. Raphael, C. Gay, P. G. de Gennes, *J.Stat.Phys.* 89, 111-118 (1997).
- [3] G. T. Pickett, *Europhys.Lett.* 76, 616-622 (2006).
- [4] M. Lang, J. Fischer, M. Werner, J.-U. Sommer, *Phys. Rev. Lett.* 112 (2014) 2380001.
- [5] M. Rubinstein, R. Colby, *Polymer Physics*, Oxford University Press, Oxford, UK (2003).
- [6] J. Bastide, C. Picot, S. Candau, *J.Macromol.Sci.Phys.* B19, 13 (1981).

Nitrile butadiene rubber/in-situ synthesized polyurethane-urea blends with improved properties

Muhammad Tahir, Regine Boldt, Maria Auf der Landwehr, Klaus Werner Stöckelhuber, Sven Wießner, Gert Heinrich

Polyurethane-ureas are high performance engineering materials that have distinguished profile of superior mechanical properties due to the range of available characteristic constituents (diisocyanates, polyols and diamines) and unique heterophase structural morphologies. The distinguished mechanical characteristics of polyurethane-ureas can be incorporated in rubbers by blending methodologies to obtain advanced multicomponent materials. However, only a few investigations have been reported on blending polyurethane-ureas with rubbers by a time and energy intensive solvent-blending method. In addition, the reported results of rubber/ polyurethane-urea blends show that the dispersed polyurethane-urea phase gets soften at high temperatures and its effect transforms from reinforcing to softening.

In the present work, a simple reactive blending method is investigated to incorporate effectively the useful characteristics of polyurethane-ureas in rubbers and to address the heat build-up concerns due to the softening of polyurethane-urea phase (Fig. 1). To follow this method, polyurethane-urea (PUU) with high content of hard segments is synthesized *in-situ* via a prepolymer route during blending with nitrile butadiene rubber (NBR) in an internal mixer [1, 2]. Subsequently, the PUU phase is solvent-extracted from blends to characterize the addition polymerization of isocyanate-terminated prepolymer with diamine by ¹H NMR spectroscopy.



Fig. 1:
Scheme of reactive blending methodology showing structure of NBR and the reactive prepolymer and diamine for the in situ PUU.

Polymere Netzwerke: Struktur, Theorie und Anwendung

After structural verification, blends are compounded with curatives on a two-roll mixing mill to get blend vulcanizates by compression moulding. Fig. 2 demonstrates the stress-strain curves of blend vulcanizates, which reflects concentration dependent reinforcement of nitrile butadiene rubber by *in-situ* synthesized PUU.

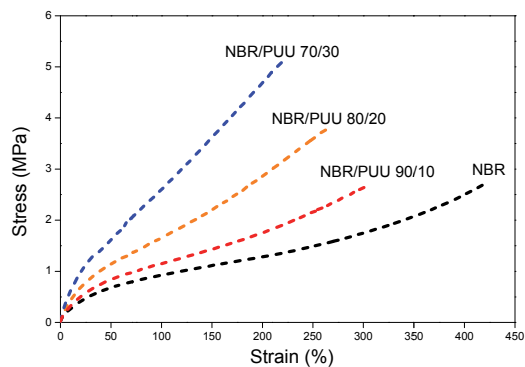


Fig. 2: Stress-Strain curves showing improvement in the tensile profile of NBR upon incremental loading with PUU.

The elastic modulus and tensile strength increase and elongation at break decreases with the loading of stiff PUU phase, which characterizes self-compatibilization of NBR/PUU blend system. The reinforced blends, as observed from the dynamic mechanical behavior of blend vulcanizates, demonstrate a progressive drop in the peak height of loss factor and a corresponding rise in the storage modulus through the NBR transition region towards a stable rubbery plateau region at high temperatures upto 180°C.

Scanning Electron Microscopy coupled with energy dispersive X-ray spectroscopic (SEM-EDX) investigation of blend vulcanizates shows oxygen-rich distinguished PUU domains dispersed in continuous NBR matrix (Fig. 3).

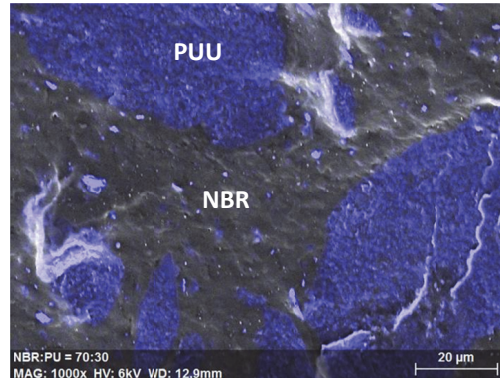


Fig. 3: SEM-EDX micrographs with elemental oxygen mapping shows oxygen-rich PUU domains (blue) dispersed in NBR matrix.

In-situ synthesized PUU domains develop strong interfacial adhesion, which prevents its delamination from continuous NBR phase on cryogenic fracturing. In addition, the roughness of interfacial boundary promotes mechanical interlocking between two distinct phases and explains the unprecedented improvement in the mechanical and dynamic-mechanical characteristics of NBR/PUU blend system. The prepared blend vulcanizates possess new profile of attractive properties and are cost-effective materials for applications like rubber rollers, belting, pump impellers, industrial wheels etc.

Co-operation:

Dr. Nasir Mahmood, Institut für Chemie,
Martin-Luther-Universität Halle Wittenberg,
Halle (Saale), Germany

- [1] M. Tahir, N. Mahmood, K.W. Stöckelhuber, G. Heinrich, A. Das, R. Jurk, German Patent Application DE 102013217661.9 & European Patent Application EP2014/068245
- [2] M. Tahir, K. W. Stöckelhuber, N. Mahmood, H. Komber, G. Heinrich: Macromol. Mater. Eng. [2014], DOI: 10.1002/mame.201400298.

Polymere Netzwerke: Struktur, Theorie und Anwendung

Keywords
soft magnetic elastomers
magneto-induced
deformation
controllable stiffness
modelling

Mechanical properties of magneto-sensitive elastomers: unification of the continuum-mechanics and microscopic theoretical approaches

Dmytro Ivaneyko, Vladimir Toshchevikov,
Marina Saphiannikova, Gert Heinrich

Magneto-sensitive elastomers (MSEs) belong to a class of smart materials due to their ability to change easily the shape and stiffness under applied magnetic field. These features make MSEs very perspective materials for design of sensors, robotics, actuators, dampers and for other industrial applications [1].

MSEs consist of micron-sized magnetic particles dispersed within a non-magnetic soft elastomeric matrix. Carbonyl iron with soft magnetic properties and high saturation magnetization is commonly used for the MSE preparation. It is possible to produce MSEs with isotropic and anisotropic spatial distribution of the particles. To produce MSEs with anisotropic particle arrangement the external magnetic field should be applied to the melt before the curing process [1,2]. It was shown experimentally that the microscopic particle distribution has a strong influence on the mechanical properties of MSEs. To describe this effect many theories have been proposed. While most of them are based on the macroscopic continuum-mechanics approach addressing the shape effects [3], a few recent studies including ours utilize the microscopic approach which describes explicitly the particle distribution [4]. To be able to predict the magneto-mechanical behavior of real MSE samples, it is necessary to combine these two approaches.

To this aim, we developed recently a rigorous theoretical formalism which allows to analyze the mechanical behavior of the MSEs with different shapes and different particle distributions [5]. The MSE sample is considered as an ellipsoid of revolution with the aspect ratio $\gamma = A/B$ (see Fig. 1) that contains magnetic particles with isotropic or anisotropic spatial distribution.

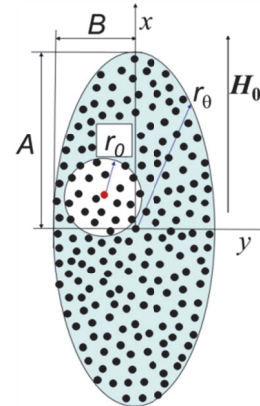


Fig. 1: Microscopic model of an MSE under a uniform external magnetic field H_0 , applied along the x -axis. A and B are the semi-axes of rotational ellipsoid, r_0 is the radius of microsphere. The function r_θ defines the boundary of the ellipsoid.

The spatial distribution of particles is characterized by the anisotropy parameter α , which is defined as the ratio of the average distances between neighboring particles along x - and y -directions. To calculate the magnetic field in a given point inside the sample (red point in Fig. 1), we introduce a microsphere of radius r_0 around this point. The value of r_0 is chosen to be much larger than an average distance between neighboring particles. Thus, the magnetic field contains contributions from the particles that are inside and outside of the microsphere. We show that the first contribution depends only on the local particle distribution, while the second contribution depends only on the shape of the sample γ . Constructing the free energy of MSE as a sum of elastic and magnetic free energies, where the latter depends now on the shape parameter γ and anisotropy parameter α , we calculate a magneto-induced deformation ε and a change of the elastic modulus ΔE : $\varepsilon = K_\varepsilon \mu_0 H_0^2 / 2E_0$ and $\Delta E = K_E \mu_0 H_0^2 / 2$. Here μ_0 is the permeability of vacuum, E_0 is the modulus in the absence of field. The coefficients of proportionality K_ε and K_E are functions of the initial aspect ratio γ_0 and the structural parameter α as shown in Fig. 2.

Polymere Netzwerke: Struktur, Theorie und Anwendung

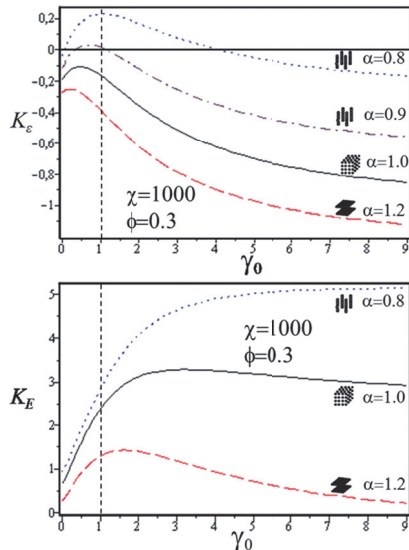


Fig. 2:
The coefficients K_ε and K_E as functions of the initial aspect ratio of the sample γ_0 , calculated for the chain-like ($\alpha = 0.8, 0.9$), isotropic ($\alpha = 1.0$) and plane-like ($\alpha = 1.2$) structures, modeled on the hexagonal close-packed lattice. The volume fraction $\phi = 0.3$ and magnetic susceptibility of particles $\chi = 1000$.

In particular, we found that the magneto-induced deformation and the change of the elastic modulus can be either positive or negative, depending on the initial shape of the MSE sample and on the local spatial distribution of particles. Besides, the effect of the mechanical coupling between the particle arrangement and the sample deformation has been considered. The absence of this coupling leads to a pure macroscopic approach, whereas the presence of the strong coupling leads to the main contribution of the microscopic approach [5].

Sponsor:

The current work was supported from the funds of the DFG grant GR 3725/6-1.

Co-operation:

Dr. Dmitry Borin, Dr. Markus Kästner
Technische Universität Dresden

- [1] G. Filipcsei, I. Csetneki, A. Szilágyi, M. Zrínyi: *Advances in Polymer Science* 206 (2007) 137-189
- [2] C. Hintze, D. Y. Borin, D. Ivaneyko, V. Toshchevnikov, M. Saphiannikova, G. Heinrich: *Kautschuk Gummi Kunststoffe* 67/4 (2014), 53 - 59
- [3] Y. L. Raikher, O. V. Stolbov: *Technical Physics Letters* 26 (2000), 156-158
- [4] D. Ivaneyko, V. Toshchevnikov, M. Saphiannikova, G. Heinrich: *Macromolecular Theory and Simulations* 20 (2011), 411-424
- [5] D. Ivaneyko, V. Toshchevnikov, M. Saphiannikova, G. Heinrich: *Soft Matter* 10 (2014), 2213 - 2225

Polymere Netzwerke: Struktur, Theorie und Anwendung

Keywords
polymer-matrix
composites
fracture toughness
particle size distribution

Effect of plastic void growth around particles with a size distribution on toughness of polymer composites

Bernd Lauke

1. Introduction

Crack resistance of particle reinforced polymers is affected by the size distribution of particles. Dissipation mechanisms, as particle debonding, matrix shear bands or plastic voiding, are responsible for the fracture mechanical behaviour. As the energy contribution of particle debonding may depend on particle size distribution [1] also the dissipation energy caused by matrix voiding after debonding from the matrix depends on this structural parameter. The plastic void growth mechanism was modelled by Williams [2] and in Ref. [3] and is extended herein for the particle size distribution effect.

2. Crack resistance, fracture toughness

The energy necessary to initiate crack propagation is called crack resistance, R_c or toughness, respectively. During crack growth, the crack consumes energy, R_{pz} , to form the new fracture surface in the process zone. At the same time energy, R_{dz} , is dissipated by matrix yielding around debonded particles within a larger zone of width, $2\rho_y$, subsequently called the yielding zone. The zone energy is given by the product of matrix toughness, R_m , and the relevant volume fraction, v_m , plus the dissipation zone energy which is the integral over all local contributions:

$$(1) \quad R_c = R_{pz} + R_{dz} = R_m v_m + 2 \int_0^{\rho_y} \eta_{my}(\rho) d\rho$$

where η_{my} is the volume specific matrix yielding energy, ρ is the distance coordinate from the crack tip. The multiaxial stress field under remote mode I loading at the position ρ can be approximated by a uniform radial tensile stress, σ_0 : $\sigma_0(\rho) = (\beta R_c E_c / \rho)^{1/2}$ where β is a zone shape and size factor and E_c is the composite modulus. Consequently the width of the dissipation zone, ρ_y , is given by:

$\rho_y = \beta R_c E_c / \sigma_{0,\min}^2$ with $\sigma_{0,\min}$ as the minimum radial stress where plastic yielding in the matrix shell around a particle starts. The

integration over the distance, ρ , from the crack plane can be transformed into integration over the stress. With the replacement: $d\rho = -2\beta R_c E_c (\sigma_0)^{-3} d\sigma_0$ and the normalization, $s = \sigma_0 / \sigma_{my}$, the integral in Eq. (1) can be rewritten as:

$$(2) \quad R_{dz} = 4\beta R_c E_c \frac{1}{\sigma_{my}^2} \int_{s_{\min}}^{s_{\max}} \eta_{my}(s) (s)^{-3} ds$$

with σ_{my} as the matrix yield strength and s_{\min} and s_{\max} as defined below.

3. Single particle model

A spherical particle embedded within a spherical polymer matrix under uniform radial stress is considered. The geometry is shown in Fig. 1.

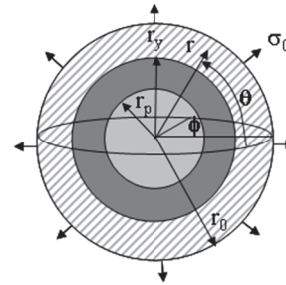


Fig. 1: Single particle, radius, r_p , within matrix material of radius, r_0 ; r_y yielding radius.

The local particle volume fraction is defined by: $\tilde{v} = (r_p/r_0)^3$. The representative element is under uniform stress, σ_0 , leading to stress concentrations, $\sigma_{ij}^m / \sigma_0 = \kappa$. Williams [2] derived the debonding stress at the particle/matrix interface as:

$$(3) \quad \sigma_{tr}^m = \sigma_d = \sqrt{8G_d E_m / (d_p (1 + v_m))}$$

with the specific debonding energy, G_d , and E_m and v_m as the matrix Young's modulus and Poisson's ratio, respectively.

Polymere Netzwerke: Struktur, Theorie und Anwendung

4. Particle size distribution

It is assumed that the Gaussian normal distribution function provides a mathematical description of the probability density, $f_n(d_p)$, for the particle size and describes more or less exactly the measured values. With f_n and the particle volume density, n_p , the particle volume fraction, v , is given by:

$$v = \frac{\pi}{6} n_p \int_{d_{p,\min}}^{d_{p,\max}} d_p^3 f_n dd_p = \frac{\pi}{6} n_p V_p.$$

The particle diameters lay between the limits $d_{p,\min}$ and $d_{p,\max}$ and the number of particles of a special size is given by: $n_j = n_p f_n dd_p$.

5. Energy of plastic voiding, crack resistance

The yielding energy is derived by the product of applied force, F_o , with displacement, Δu , at the matrix shell of radius, r_o :

$$W_{my} = F_o \Delta u = 4\pi r_o^2 \sigma_0 \Delta u.$$

This displacement was calculated in [3] to be

$$\Delta u = r_o \sigma_0 \Delta \tilde{C}(s, \tilde{v}, v_m) / E_m$$

with the functionality given therein. With this value the yielding energy of the matrix shell around one debonded particle was calculated as:

$$W_{my} = 4\pi r_o^3 (\sigma_{my} s)^2 \Delta \tilde{C} / E_m. \text{ The volume density of yielding energy is now given by:}$$

$$(4) \quad \eta_{my}(s) = n_p \int_{d_p(s)}^{d_{p,\max}} W_{my} f_n dd_p$$

The value of the lower limit of particle diameter, $d_p(s)$, results from Eq. (3) to be:

$$d_p(s) = 8G_d E_m / ((1 + v_m) \sigma_{my}^2 \kappa^2 s^2).$$

Inserting this into Eq. (2) and then into Eq. (1) provides the composite toughness to be:

(5)

$$\frac{R_c}{R_m} = \frac{v_m}{1 - \frac{12\beta E_c v}{E_m V_p} \frac{1}{\tilde{v}} \int_{s_{\min}}^{s_{\max}} \frac{1}{s} \Delta \tilde{C}(s) \left[\int_{d_p(s)}^{d_{p,\max}} d_p^3 f_n dd_p \right] ds}$$

with $s_{\min} = 2(1 - \tilde{v})/3$ and $s_{\max} = -2 \ln \tilde{v} / 3$.

6. Results

The proposed model is applied for glass-sphere-filled polyethylene with the following material properties for the spheres: $E_p = 64$ GPa, $v_p = 0.2$. The elastic properties of the polyethylene matrix are: $E_m = 520$ MPa, $v_m = 0.35$ and the matrix yield stress: $\sigma_{my} = 27$ MPa.

As can be seen in Fig. 2 the composite toughness increases at lower mean particle sizes and remains constant for larger values.

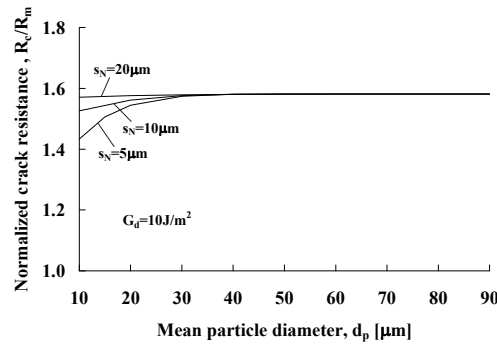


Fig. 2: Fracture toughness (crack resistance) as a function of mean particle diameter for different standard deviations, s_N , of a Gaussian normal distribution of particles of the size between $d_{p,\min} = 1 \mu\text{m}$ and $d_{p,\max} = 100 \mu\text{m}$, $v = \tilde{v} = 0.05$.

For particle size distributions with larger standard deviations, s_N , fracture toughness becomes rather independent of mean particle size. This behaviour is caused by the fact that smaller particles demand higher stresses for debonding and subsequent matrix yielding. The fraction of particles that do not debond do not induce matrix yielding in the neighbourhood.

- [1] B. Lauke: Computational Mater. Sci. 77(2013), 53-60
- [2] J.G. Williams: Comp. Sci. a. Technol. 70 (2010), 885-891
- [3] B. Lauke: Compos. Sci. and Technol. 86(2013), 135-141

Polymere Netzwerke: Struktur, Theorie und Anwendung

Keywords

PVT analysis
epoxy shrinkage
crosslinking kinetics
phase transition

PVT als Methode zur Charakterisierung von Vernetzungsreaktionen und Phasenübergängen von Polymeren und Monomeren

Jürgen Pionteck

Die Analyse der PVT-Daten von Polymeren ermöglicht nicht nur die Bestimmung des spezifischen Volumens von Polymeren in Abhängigkeit von Druck und Temperatur, sondern auch die Analyse von Phasenübergängen der Polymeren, Polymerisationen, Abbaureaktionen, Vernetzung, Umesterung und anderen Phänomenen, die mit einer Änderung des spezifischen Volumens verbunden sind. Zeitabhängige Untersuchungen erlauben die Bestimmung kinetischer Parameter.

Eine Sammlung von im IPF gemessenen PVT-Daten von kommerziellen und nichtkommerziellen Polymeren, Kompositen und Blends findet sich in [1]. Die Untersuchungen erfolgten mit einem GNOMIX-PVT-Dilatometer (GNOMIX Inc., Boulder, CO 80304, USA), das eine Genauigkeit von 0,002 cm³/g (oberhalb 240 °C von 0,004 cm³/g) bei der Bestimmung des spezifischen Volumens (V_{sp}) im Druck- und Temperaturbereich bis 200 MPa bzw. 400 °C ermöglicht, wobei Änderungen im spezifischen Volumen bei konstantem Druck und Temperatur von 0,0002 cm³/g nachweisbar sind. Derartige Daten werden benötigt, um die Kompressibilität, die thermische Ausdehnung und die Temperatur von Phasenübergängen in Abhängigkeit vom Druck und von der thermischen Vorgeschichte der Materialien zu erhalten. Abb. 1a zeigt Daten eines Polycarbonats, gemessen als Isotherme unter Druckaufbau von 10 bis 200 MPa bei jeder Temperatur.

Der Bereich zwischen den beiden Geraden ist instabil und die Abweichung von den Isobaren (Abb. 1b, die Gerade kennzeichnet hier die Abhängigkeit der Glasübergangstemperatur vom Druck) wird durch den Glasübergang während des Druckaufbaus verursacht. Solche Daten werden z.B. für die Modellierung des Spritzgussprozesses benötigt.

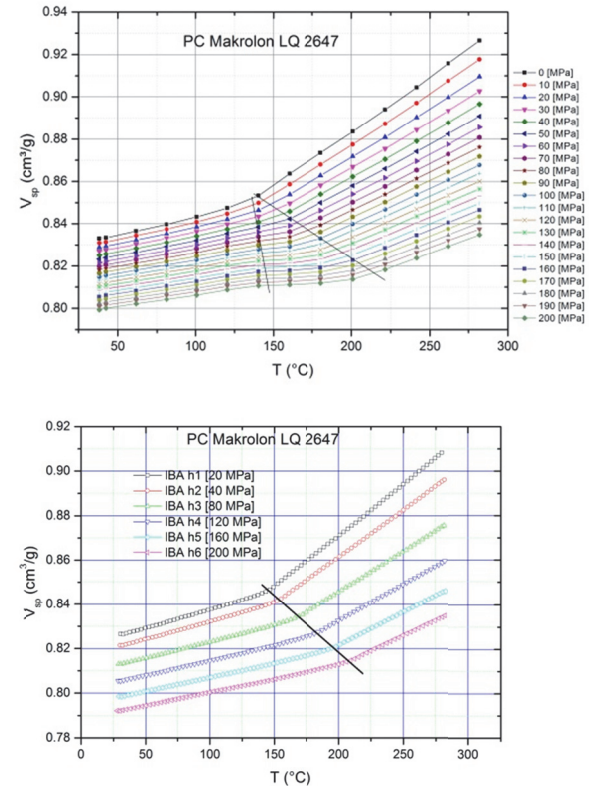


Abb. 1:
PVT-Daten von Polycarbonat, erhalten über isotherme (a) oder isobare (b) Messungen

In reaktiven Systemen lässt sich der Verlauf der Umsetzung anhand des Schrumpfes des Materials, verursacht durch Polymerisation oder Vernetzung, verfolgen. Bei der Modifizierung eines Epoxids mit SiC-Nanofasern und carboxylterminiertem Poly(butadien-co-acrylonitril)-Kautschuk (CTBN) wurde nachgewiesen, dass die Art der Probenpräparation einen deutlichen Einfluss auf die thermische Stabilität und die Vernetzungsdichte hat. Werden die SiC-Nanofasern erst mit dem Epoxidharz gemischt und dann der CTBN-Kautschuk eingemischt (M2), werden bessere Werte erhalten als beim gemeinsamen Mischen aller drei Komponenten vor der Härtung (M1). Auch der Volumenschrumpf ist bei Methode 2 um 10 % verringert (Abb. 2).

Polymere Netzwerke: Struktur, Theorie und Anwendung

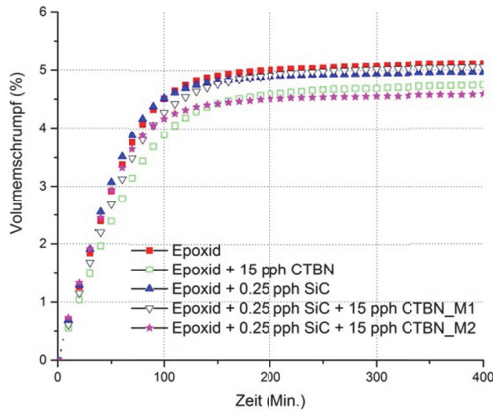


Abb. 2:
Einfluss von SiC-Nanofasern und CTBN-Kautschuk sowie der Verarbeitungsmethode auf die Vernetzungskinetik und den Volumenschrumpf eines Epoxids, analysiert mittels PVT-Dilatometer (10 MPa, Abbildung aus [2] adaptiert).

SiC beschleunigt die Vernetzung, während CTBN diese etwas verlangsamt, jedoch die Zähigkeit des Epoxids erhöht [2].

Auch in niedermolekularen Verbindungen beeinflusst das freie Volumen, bestimmbar durch Anpassen der gemessenen PVT-Parameter an Phasenzustandsgleichungen (z.B. Simha-Somczynski-Phasenzustandsgleichung) die Beweglichkeit der Moleküle und ihre Phasenübergänge sowie die elektrische Leitfähigkeit. Die Druckabhängigkeit der Glasübergangstemperatur bestimmt über PVT-Analyse oder dielektrische Spektroskopie stimmt für die protische ionische Flüssigkeit Carvediloldihydrogenphosphat gut überein [3]. Ein Vergleich der beobachteten Strukturrelaxationen mit druckabhängigen Viskositätsdaten und elektrischen Leitfähigkeiten erlaubt Rückschlüsse auf den Leitfähigkeitsmechanismus von dieser ionischen Flüssigkeit.

Kooperationen:

Prof. S. Thomas, Mahatma-Ghandi-Universität
Kottayam, Indien;

Prof. M. Paluch, University of Silesia, Katowice,
Poland

- [1] J. Pionteck, M. Pyda: Thermodynamic Properties – pVT-Data and Thermal Properties; in K.-F. Arndt, M. D. Lechner (Edts): Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology- New Series, Group VIII: Advanced Materials and Technologies, Volume 6: Polymers, Subvolume A: Polymer Solids and Polymer Melts, Part 2, Springer, Heidelberg 2014
- [2] P. Poornima Vijayan, J. Pionteck, A. Huczko, D. Puglia, J. M. Kenny, S. Thomas: Liquid rubber and silicon carbide nanofiber modified epoxy nanocomposites: Volume shrinkage, cure kinetics and properties; *Comp. Sci. Tech.* 102 (2014) 39-46.
- [3] Z. Wojnarowska, Y. Wang, J. Pionteck, K. Grzybowska, A. P. Sokolov, M. Paluch: High Pressure as a Key Factor to Identify the Conductivity Mechanism in Protic Ionic Liquids, *PRL* 111, 225703 (2013)

Polymere Netzwerke: Struktur, Theorie und Anwendung

Keywords

polymer networks
linear dynamic moduli
multiscale approach
statistical-physical theory

Multiscale approach to dynamic-mechanical analysis of unfilled rubbers

Marina Saphiannikova, Vladimir Toshchevikov, Igor Gazuz, Gert Heinrich

The understanding of the relationship between the dynamic-mechanical properties of polymers and their molecular structure has considerably improved with the development of molecular dynamics theories. Besides the academic interest of molecular theories, the accurate description of the structure/property relationships is of the highest importance for the polymer and rubber industry, as the processing as well as final properties of polymer products are directly governed by their dynamic-mechanical behaviour. Nowadays, the linear dynamic-mechanical properties of entangled polymer melts can be represented reasonably well using a multiscale approach which combines different relaxation regimes: glassy regime at very high frequencies, followed by Rouse regime at the intermediate frequencies and reptation regime at low frequencies [1]. However, a physically motivated multiscale approach similar to that used for the polymer melts has not been yet applied to the crosslinked networks.

Recently we elaborated a versatile theoretical multiscale approach for description of the linear dynamic moduli of the randomly crosslinked polymer networks across a broad frequency domain [2]. The frequency-dependent dynamic moduli in the multiscale approach are calculated on the base of the logarithmic spectral density function of the relaxation times $H(\tau)$. This function has the form of a piecewise-power-law (see insert of Fig.1) that combines the ideas developed in the statistical-physical theory of polymers for different frequency regimes: (1) nonpolymeric relaxation processes at extremely high frequencies, (2) the bending modes of the polymer chain at high frequencies, (3) the Rouse relaxation processes at intermediate frequencies, and finally (4) extremely long-time relaxation processes at low frequencies.

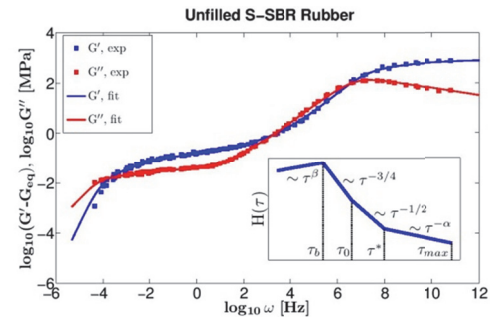


Fig. 1: Fits of the master curves for the storage and loss moduli for the unfilled S-SBR rubber with the multiscale approach. Insert shows schematically the logarithmic spectral density $H(\tau)$ in which four different regimes are separated by the characteristic relaxation times.

The structural origin of the long-time relaxation regime is still a matter of discussion in literature. Comparing the form of the long-time relaxation spectrum with different theoretical approaches, we conclude that this spectrum is caused by a slow reptation dynamics of dangling chains [3]. The proposed multiscale approach allows us to interpret experimental data based on structural characteristics of polymer materials as the length of the Kuhn segment, the numbers of Kuhn segments in an entangled fragment, in the active network strands between junctions and in dangling chains as well as the volume fractions of active chains and dangling material.

Only after taking into account this richness in relaxation processes on various time and length scales, an excellent description of dynamic moduli of unfilled rubbers was achieved. Fig. 1 shows exemplarily the relaxation part of the storage modulus, $G' - G_{eq}$, and the loss modulus, G'' , as functions of the angular frequency ω for the unfilled S-SBR rubber crosslinked with 1 phr sulfur. Here G_{eq} is the plateau modulus which corresponds to the limiting value of the storage modulus at low frequencies. Structural parameters of S-SBR rubbers - the cross-link density and the density of entanglements - have been obtained from the fitting of stress-strain dependences using the extended tube model of the rubber elasticity [4]. The values of other material parameters have been

Polymere Netzwerke: Struktur, Theorie und Anwendung

extracted from the fits and are found to correlate well with the actual values for the S-SBR copolymer used in the studied samples. So, we extract the molar mass of the Kuhn segment $M_s \approx 300$ g/mol, which is in close agreement with the value $M_s = 353$ g/mol, obtained from the mathematical analysis of the chemical structure of S-SBR [5].

The newly proposed multiscale approach allows to fit and to describe the dynamic moduli of unfilled S-SBR rubbers over 16 frequency decades with a limited set of parameters (relaxation times, scaling exponents). All parameters have a clear physical meaning and obey the relations motivated by the statistical-physical theory of polymer melts and polymer networks. The multiscale approach can be generalized for the case of filled polymer networks, which is of extraordinary importance for the tire applications in automobile industry.

Co-operation:

Dr. Stephan Westermann and Dr. Frank Petry,
Goodyear Innovation Center Luxembourg

- [1] O. Bytner, G.D. Smith: *Macromolecules* 34 (2001), 134-139
- [2] M. Saphiannikova, V. Toshchevikov, I. Gazuz, P. Petry, S. Westermann, G. Heinrich: *Macromolecules* 47 (2014), 4813-4823
- [3] J.G. Curro, D.S. Pearson, E. Helfand: *Macromolecules* 18 (1985), 1157-1162
- [4] M. Kaliske, G. Heinrich: *Rubber Chem. Technol.* 72 (1999), 602-632
- [5] B. Huneke, M. Klüppel: *Kautsch. Gummi Kunstst.* 59 (2006), 242-250