Polymere Netzwerke:
Struktur, Theorie und Anwendung

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Durch die Vernetzung von Polymeren werden Flüssigkeitseigenschaften (Viskosität) mit Festkörpereigenschaften (Formbeständigkeit, Lösungsmittelbeständigkeit) kombiniert. Am IPF zeichnet sich die Forschung im Bereich der vernetzten Polymere durch eine enge Zusammenarbeit von Theorie, Simulation, Experiment und Anwendung aus und umfasst alle Programmbereiche.

Neben der hochreversiblen Elastizität ist die hohe Quellfähigkeit von Polymernetzwerken interessant. In Superabsorbern wird diese Eigenschaft ausgenutzt um wässrige Flüssigkeiten in der Größenordnung des Hundertfachen der Ausgangsmasse des Netzwerkes aufzunehmen. Für die konkreten Eigenschaften dieser Superabsorber-Netzwerke ist die Struktur des vernetzten Systems, bedingt durch die eingesetzten Syntheseprozesse, von Bedeutung. Die Aufklärung der Zusammenhänge zwischen Synthese, Struktur und Quellungseigenschaften kann über Computer-Simulationen, insbesondere auch unter Benutzung von hocheffizienten vergröberten Modellen, erfolgen (Polymer 82 (2016) 138). Materialien, die Polymere und Füllstoffelemente kombinieren, spielen eine große Rolle für Anwendungen, bei denen hohe Festigkeit und Elastizität erforderlich sind. Gerade bei hohen Belastungen sind die viskoelastischen Eigenschaften von Polymeren nichtlinear und zeigen oft das typische Verhalten der Scherverdünnung. Für diesen Fall ist die Auswirkung von Füllstoffelementen auf die mechanischen Eigenschaften nicht auf einfache theoretische Modelle rückführbar. Numerische Berechnungen können das nichtlineare elastische Verhalten der Polymermatrix in Form von einfachen Modellannahmen integrieren und Vorhersagen über das erwartete Verhalten der gefüllten Systeme machen (J. Non-Newtonian Fluid Mech. 221 (2015) 95). Essenziell für die anwendungstechnischen Eigenschaften partikelverstärkter Elastomerblends, z. B. in der Reifenindustrie, sind Füllstofflokalisierung und phasenspezifische Wechselwirkung zwischen den Kautschukkomponenten und der Füllstoffoberfläche. Durch das thermodynamisch motivierte Konzept der selektiven Füllstoffbenetzung können Voraussagen zu spezifischen Füllstoff-Kautschuk-Wechselwirkungen getroffen werden und vertiefen das Prozessverständnis für während des technologischen Kautschukmischprozesses auftretende Phänomene, wie z. B. Füllstofftransfer oder die Wirkung von Dispersionshilfsmitteln (Polymer 105 (2016) 284). Durch einen Sol-Gel-Prozess in einer SSBR-Kautschuklösung in situ gebildete Silicananopartikel ermöglichen die Herstellung von hochverstärkten Elastomeren mit exzellenter Füllstoffdispersion und optimierten dynamisch-mechanischen Eigenschaften (RSC Advances 6 (2016) 33643).

Bürsten-Polymere, bei denen eine Hauptkette eine hohe Dichte von Seitenketten aufweist, haben das Potenzial zur Erzeugung neuartiger, ultraweicher Netzwerke und Gele. Der Grund hierfür ist die Vermeidung von Verschlaufungen mit anderen Ketten, selbst in dichten Systemen, was auch zu besonderen Eigenschaften der Schmelzen führt (Science Advances 2 (2016) e1601478).

Die Entwicklung, Herstellung und Charakterisierung funktionaler und smarter Elastomere im anwendungsorientierten Bereich des ST3 innerhalb der Abteilung „Elastomere" unter der Leitung von Jun.-Prof. Sven Wießner widmet sich vor allem auch verarbeitungsrelevanten Fragestellungen, die im Rahmen öffentlich geförderter Vorhaben und Industrieprojekte bearbeitet wurden. Ein Beispiel hierfür ist das AiF-IGF Projekt „Hybridgarnbasierte Elastomerbauteile". Für seine Dissertation über zinkhaltige Nitrilkautschuk-Elastomernanokomposite wurde Dr. Debdipta Basu mit dem Förderpreis der Deutschen Kautschuk-Gesellschaft ausgezeichnet.

Polymere Netzwerke: Struktur, Theorie und Anwendung

Growth factor delivery from adhesive polyelectrolyte complex nanoparticle coatings

Martin Müller, Birgit Urban, David Vehlow, Mieke Luisa Möller

Recently highly specific proteinogenic growth factors have been integrated directly or via drug delivery systems (DDS) into biomaterials for hard tissue regeneration. However, fabricating appropriate DDS for growth factors in bone regeneration remains challenging, due to uncontrolled burst release and high doses needed to elicit biological responses [1]. Herein we describe an adhesive local drug delivery system for osteoinductive bone morphogenetic protein 2 (BMP-2) based on coatings of polyelectrolyte complex (PEC) nanoparticles (NP) [2]. Nanoparticular ternary complexes of cationic and anionic polysaccharides and BMP-2 were prepared under variation of the molar mixing ratio, pH and cationic polysaccharide. As further proteins (PROT) chymotrypsin (CHY) and papain (PAP) were selected serving as model proteins for BMP-2 due to similar isoelectric points and molecular weights. As polysaccharides ethylenediamine modified cellulose (EDAC), trimethylammonium modified cellulose (PQ10) and cellulose sulphate (CS) were used.
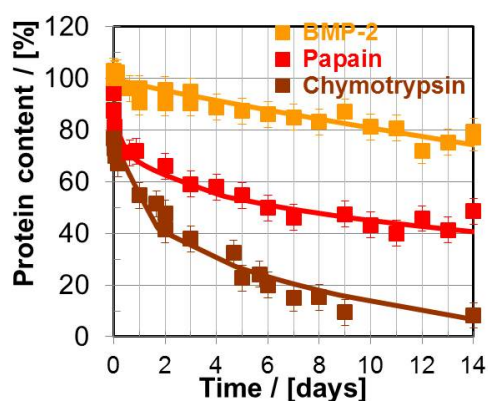

Fig. 1.:
Time dependent release of the proteins CHY, PAP and BMP-2 from ternary EDAC/CS/PROT coatings at HEPES buffer as measured by FTIR spectroscopy [2].

Mixing diluted EDAC or PQ10, CS and PROT solutions according to a slight anionic excess charge colloidally stable dispersions formed

with hydrodynamic radii of $R_H \approx 150$ nm (EDAC/CS/PROT) and $R_H \approx 220$ nm (PQ10/CS/PROT) based on dynamic light scattering. Fourier Transform Infrared (FTIR) measurements showed, that cast PEC NP/PROT coatings were irreversibly adhesive at model substrates in contact to HEPES buffer and solely CHY, PAP and BMP-2 were released within long-term periods. Advantageously, out of the three proteins BMP-2 showed the smallest initial burst and the slowest release kinetics and around 25 % of the initial BMP-2 content were released within 14 days (Fig. 1). Released BMP-2 showed significant activity in myoblast cells indicating the ability to regulate the formation of new bone (Fig. 2).
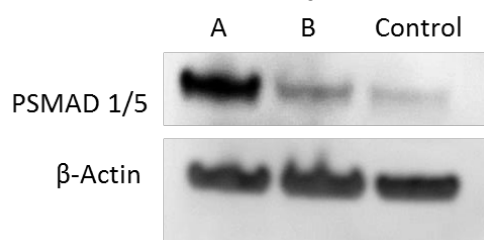

Conclusively, BMP-2 loaded PEC NP is a promising concept for the functionalization of biomaterials used for the therapy of bone defects.

[1] E. Migliorini, A. Valat, C. Picart, E.A. Cavalcanti-Adam. Cyt. Growth Factor Rev. 2015, 27, 43.
[2] R. Petzold, D. Vehlow, B. Urban, A.L. Grab, E.A. Cavalcanti-Adam, V. Alt, M. Müller. Coll. Surf. B. 2016 DOI: 0.1016/j.colsurfb.2016.11.029.

Fig. 2.:
Western blot showing Smad1/5 phosphorylation and β-actin levels in mouse myoblasts upon stimulation with BMP-2 released from pure BMP-2 film (A), BMP-2 released from EDAC/CS/BMP-2 films (B) versus control [2]

Polymere Netzwerke: Struktur, Theorie und Anwendung

Mikrofluidische Darstellung definierter Mikrogele für biotechnologische Anwendungen

Julian Thiele

Die genaue Kontrolle über Größe, Form und Zusammensetzung von Mikroemulsionen in mikrofluidischen Flusszellen und der synthetische Zugang zu maßgeschneiderten Polymervorstufen erlaubt die Anwendung der Tropfen-Mikrofluidik zur Darstellung von Templaten für Polymermikrogele mit definierten mechanischen wie physikochemischen Eigenschaften. Insbesondere die Einstellung von Quellverhalten, Stimuli-Sensitivität und Elastizität hat wesentlich zur Anwendung von Mikrogelen als 3D-Zellkulturen sowie Sensoren und Aktoren beigetragen. Hierbei ist es essentiell, mögliche Inhomogenitäten der Netzwerkmechanik auf den Mikrogelen entsprechenden Längenskalen zu untersuchen. Anstelle von gemittelten Daten aus makroskopischen Partikel-ensemble-Untersuchungen, erfolgte die routinemäßige Charakterisierung von Mikrogelen daher mittels Colloidal Probe-AFM (Abb. 1) [1].

Im Bereich der zellfreien Biotechnologie ermöglicht das Wissen um diese mechanischen wie weitere physikochemischen Eigenschaften einzelner Mikrogele die Entwicklung mikroskopischer Plattformen zur Durchführung zellfreier Biosynthesen. Hierbei konnten erstmals wesentliche Eigenschaften lebender Zellen wie Größe, räumliche Zusammensetzung sowie natürliche Dichte des Zellinnern in einer zellfreien Umgebung nachgebildet werden [2]. Hierzu wurden Polysaccharid-basierte Mikrogele mit definierter Größe und Porosität aus Mikroemulsionstemplaten produziert, mit DNA funktionalisiert und anschließend mit allen nötigen Komponenten einer zellfreien Proteinsynthese-Maschinerie beladen. Diese übersetzte die Mikrogel-immobilisierte DNA in ein funktionales Protein. Weitere Untersuchungen zeigten, dass die Nachahmung der dichten Packung des natürlichen Zellinnern mit Makromolekülen durch Beladung der Mikrogele mit Ficoll zu einer wesentlichen Steigerung der Reaktionskinetik von DNA-Transkription (Abb. 2) sowie DNA-Translation

gegenüber herkömmlichen makroskopischen Experimenten in verdünnter Lösung beitrug.
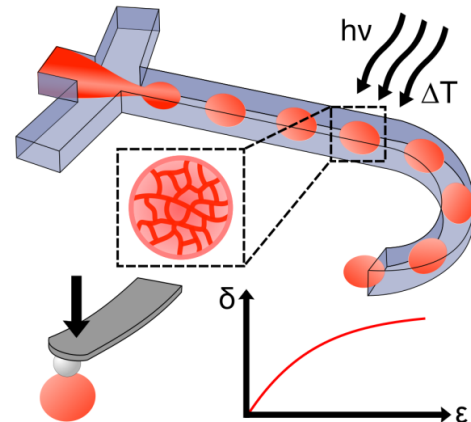

Abb. 1:

Mikrofluidische Darstellung von mikroskopischen Hydrogelpartikeln mittels On Chip-Polymerisation von Wasser-in-Öl-Emulsionstropfen sowie deren mechanische Charakterisierung mittels Colloidal Probe-AFM
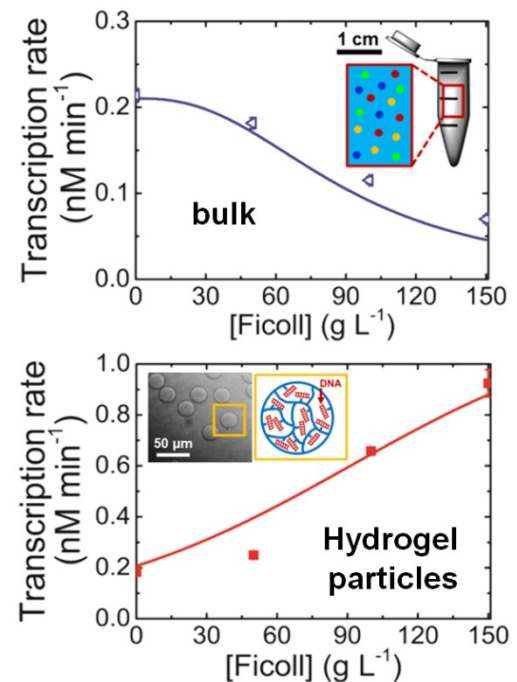

Abb. 2:

Abbildung der natürlichen Dichte des Zellinneren in vitro durch Zugabe des Makromoleküls Ficoll und sein Einfluss auf die Transkriptionskinetik in herkömmlicher, makroskopischer Lösung (oben) im Vergleich zu einer zellähnlichen Umgebung basierend auf Mikrogelen (unten).

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[1] T. Heida, J. W. Neubauer, M. Seuss,
     N. Hauck, J. Thiele, A. Fery: Macromol.
     Chem. Phys. 2016, 10.1002/macp.
     201600418.
[2] M. M. K. Hansen, S. Paffenholz,
     D. Foschepoth, H. A. Heus, J. Thiele,
     W. T. S. Huck: ChemBioChem 2016, 17,
     228-232.

Selective wetting and phase specific localization of fillers in rubber blends

Hai Hong Le, Sven Wießner, Gert Heinrich

The phase specific localization of reinforcing and/or functional nanofillers in rubber blends is a decisive factor which determines the physical and application relevant properties of the final rubber vulcanizates. With the so called *wetting concept*, developed in our previous work, the specific interaction between individual rubber components and the filler surface, called selective wetting, can be characterized and thus the phase specific localization of the fillers within the blend phases can be predictted. In the current project this *wetting concept* was further developed and applied for the characterization of the selective filler wetting in rubber blends and to describe the effectiveness of additional dispersion agents.
In the first part, based on atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR) analysis of the rubber-filler gel (*wetting concept*), the kinetics of selective wetting of carbon nanotubes (CNTs) in ternary styrene butadiene rubber (SBR)/ butadiene rubber (BR)/natural rubber (NR) blends was qualitatively and quantitatively characterized [1]. Almost all CNTs are found to be wetted by the non-polar NR but not by the non-polar rubbers like BR or weakly polar SBR. It was proposed that phospholipids, which are linked to the α-terminal of NR, can interact with the CNT surface through cation-π interactions forming relatively strong bonding between NR and CNTs. By replacing the non-polar BR by a polar rubber like nitrile butadiene rubber (NBR) as a blend component the CNTs are wetted by NBR somewhat more compared with NR due to the stronger interaction between CNTs and nitrile groups of NBR. SBR remains unbound to CNTs in both blends.
In the second part of the project, the *wetting concept* was adapted for characterization of the selective wetting behavior of silica in a miscible rubber blend from emulsion styrene butadiene rubber (ESBR) and solution styrene butadiene rubber (SSBR) blends [2]. It was found that not only the chemical rubber-filler affinity but also the topology of the filler surface significantly influences the selective filler
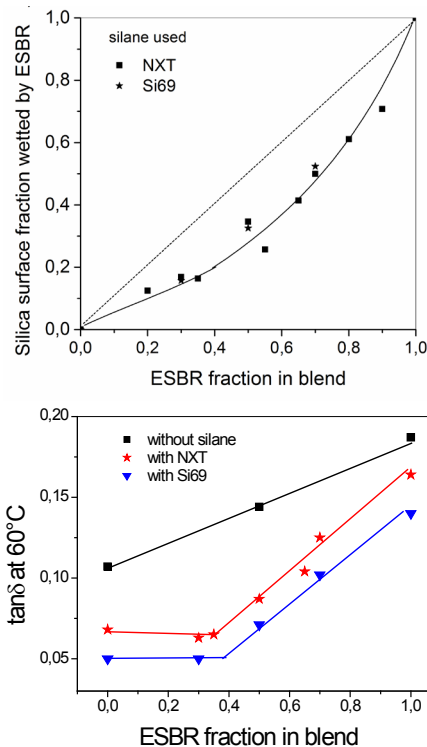
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wetting in rubber blends. The nanoporous structure of the silica surface has been recognized as the main reason for the difference in the wetting behavior of the branched ESBR molecules and linear SSBR molecules. However, the effect of nanoporous structure becomes more significant in the presence of a silane coupling agent. It is discussed that the adsorption of silane on silica surfaces constricts the nanopores to some extent hindering effectively the space filling of the nanopores by the branched ESBR molecules but not by the linear SSBR molecules. As a result, in silanized ESBR/SSBR blends the dominant wetting of silica surface by the tightly bonded layer of SSBR molecules causes a low-energy dissipation in the rubber-filler interphase. From application point of view in the tire industry, this concept imparts a low rolling resistance similar to that of silica-filled SSBR compounds (low tanδ –values), while the ESBR-rich matrix warrants the good tensile behavior, i.e., good abrasion and wear resistance of the blends (Fig. 1).

compounds was investigated [3]. It was found that DMIC shows a good compatibility to SBR and improves the CNT dispersion significantly. A DMIC layer, which is physically pre-bound to the CNT surface, is partly or completely replaced by the SBR molecules during mixing as a result of thermodynamic driving forces (Fig. 2). Subsequently the filler network formation of CNTs in SBR, NR, and IR and its effect on the electrical and mechanical properties of the compounds was characterized and discussed considering the selective wetting of CNT surface [4].
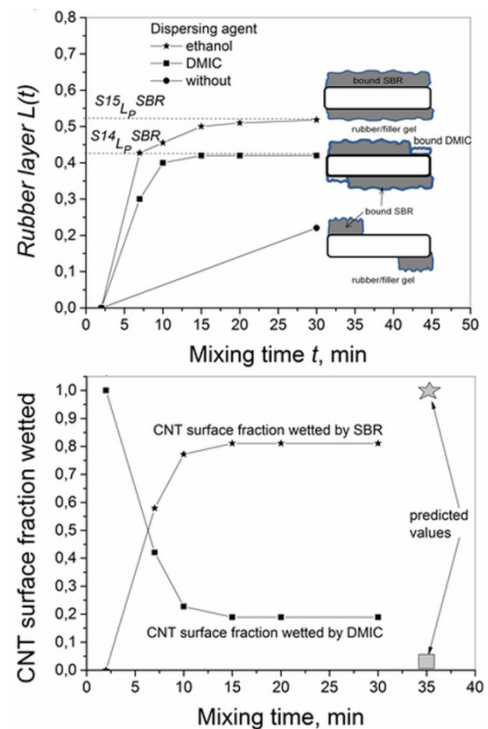

Fig. 1:
(a) Selective wetting of silica surface by SSBR in silanized ESBR/SSBR-blends: Surface fraction wetted by SSBR and (b) tanδ at 60°C as indicator for rolling resistance of a tire tread compound [2]

Fig. 2:
(a) Rubber layer L of ethanol/CNT/SBR, DMIC/CNT/SBR and CNT/SBR compound in dependence on mixing time, (b) selective wetting of CNT surface by SBR and DMIC in DMIC/CNT/SBR compound during mixing process [3]

In the third part, the role of a ionic liquid, 1-decyl 3-methyl immidazolium chloride (DMIC) as dispersing and coupling agent in CNT/SBR

In the fourth part, the effect of different ionic liquids (ILs) with various anions and alkyl chain length on the properties of CNT filled SBR/NR blends was studied [5]. ILs where characterized by their surface tensions which explain the different compatibilities of ILs with the rubber components and the filler. The *wetting concept* was applied to experimentally characterize the effect of the rubber-IL and CNT-IL compatibility on the selective wetting of CNTs in rubber

blends. It was found that all the used ILs improved the dispersion of CNTs in the blends significantly. During the mixing process the IL layer pre-bound to the CNT surface was replaced mainly by the NR phase and, partly, by the SBR phase. Thus, ILs cannot be used as coupling agent in this rubber blend. For the ILs with surface tension similar to that of CNTs the filler was partly wetted by IL that imparts the mixture a high electrical conductivity directly after the mixing process. This high conductivity can be used for triggering the vulcanization of the blend by means of Joule heating. The preferential localization of ILs in the rubber matrix - but not in rubber-filler interphase - considerably influences the cross-linking behavior of the vulcanizates and thus their final mechanical properties significantly.
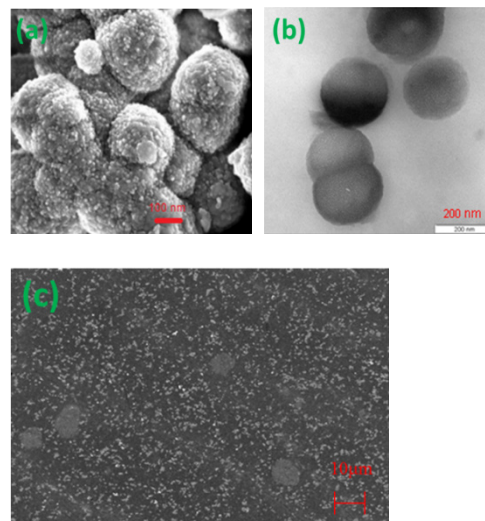
Co-operation:
Prof. A. Bhowmick, Indian Institute of Technology Kharagpur, India

[1]   H. H. Le et al., eXPRESS Polym. Lett. 9 (2015) 960–971.
[2]   H. H. Le et al., Macromol. Mater. Eng. 301 (2016) 414-422.
[3]   H.H. Le et al., Europ. Polym. J. 75 (2016) 13–24.
[4]   H.H. Le et al., Polymer 73 (2015) 111-121.
[5]   H. H. Le et al., Polymer 105 (2016) 284-297.

Reinforcement of SSBR by in-situ synthesized sol-gel silica particles

Sankar Raman Vaikuntam, Amit Das,
Klaus Werner Stöckelhuber, Sven Wießner,
Gert Heinrich

The tire industry is constantly searching for improved materials to solve current environmental issues like lower CO_2 emission, lower fuel consumption and safety aspects as well. Silica reinforced rubbers are one of the important materials playing a major role here due to their potential to lower rolling resistance and improve wet skid resistance [1]. Some of major issues encountered using silica as high performance fillers are their difficult dispersion, strong flocculation tendency and thus a difficult controllable and adjustable Payne effect. Considering above consequences, we prepared silica based rubber composites adapting the in-situ sol-gel method [2]. In our work the silica particles are synthesized inside a solution of styrene butadiene rubber (SSBR) by using tetraethoxyorthosilicate (TEOS) as a silica precursor and n-butylamine as a catalyst. The generated in-situ silica particles exhibit a size of 200-400 nm and can be well dispersed in the rubber matrix in a subsequent compounding step in the internal mixer [3]. Fig. 1a shows the SEM morphology of in-situ silica powder removed from the un-vulcanized rubber and Fig. 1b shows the TEM and SEM images of in-situ silica filled SSBR composites.

Fig. 1:
(a) SEM images of in-situ derived silica particles removed from the unvulcanized rubber, (b) and (c) TEM and SEM images of in-situ silica based rubber composites

The prepared in-situ silica composites offered excellent mechanical and dynamic mechanical properties, a lower heat build-up, higher resilience and improved crack resistance properties even without silanization by addition of TESPT silane coupling agent. The addition of a silane coupling agent in the in-situ silica composites further enhances the performance of the rubber, especially the stress-strain-properties without deteriorating the important dynamic mechanical properties. When compared with silane modified commercial silica based rubber composites the perspective tire performance of the in-situ silica composites is significantly improved in terms of lower rolling resistance (lower $\tan\delta$-values at 60°C), but good wet grip and ice grip properties (higher $\tan\delta$-values in the relevant frequency range). Fig. 2a and 2b show the $\tan\delta$ spectra as an indicator for tire properties.

For the high level of mechanical properties of the in-situ silica SSBR-composites even in the non-silanized case we provide the following explanation: The synthesis of the in-situ silica particles in presence of the solved rubber polymers allows for trapping of some of the polymer molecules within the filler aggregates as well as strong mechanical tethering of the polymer chains on the silica surface. These domains act as additional crosslinking points, therefore, offer exceptional mechanical reinforcement to the rubber without silane. The pictorial representation of the proposed in-situ silica formation and plausible rein¬forcement mechanism is shown in Fig. 3.
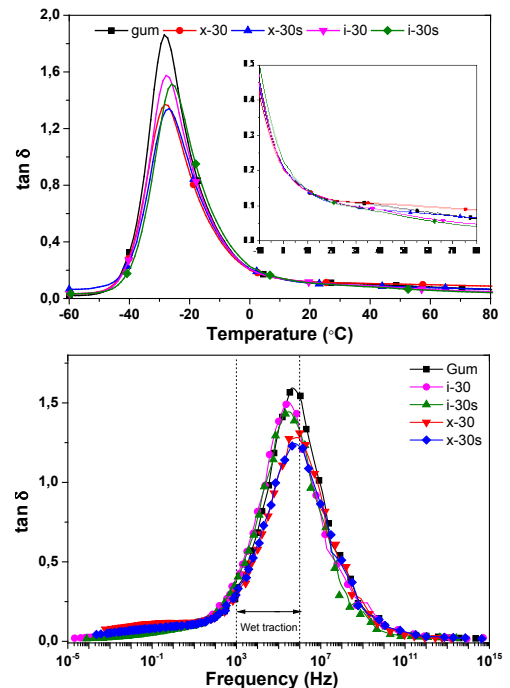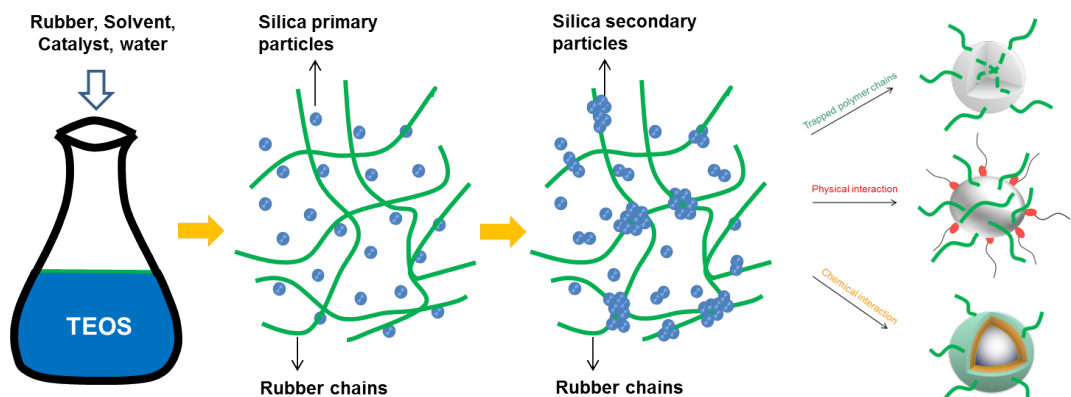

Fig. 2.:

(a) $\tan\delta$ vs. temperature and (b) $\tan\delta$ vs. frequency of 30 phr filled in-situ silica and commercial silica-SSBR composites

[1] G. Heinrich, T. Vilgis, KGK. Kautschuk, Gummi, Kunststoffe, 2008, 61.
[2] A. Das, R. Jurk, K. W. Stöckelhuber, G. Heinrich, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, 2007, 45, 101-106.
[3] V. S. Raman, A. Das, K. W. Stöckelhuber, S. B. Eshwaran, J. Chanda, M. Malanin, U. Reuter, A. Leuteritz, R. Boldt, S.Wiessner, G. Heinrich, RSC Advances, 2016, 6, 33643-33655.

Fig. 3.:
Schematic representation of in-situ silica formation inside the rubber solution, formation of primary and secondary particles and their reinforcement mechanism

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Modification of the Bird-Carreau model for dilute suspensions of spherical particles
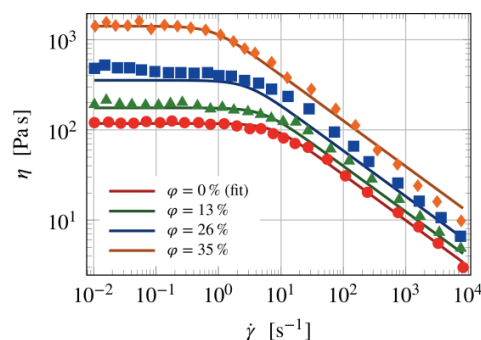
Jan Domurath, Marina Saphiannikova, Gert Heinrich

More than 100 years ago Albert Einstein computed in his dissertation the change in viscosity of a dilute suspension of rigid spherical particles as $\eta^* = \eta(1 + 2.5\varphi)$. Here η is the viscosity of the matrix fluid and φ is the volume fraction of particles. A main assumption in the calculation of Einstein is that the fluid is Newtonian, that is its viscosity η is constant. If one looks at conventional polymers, as used in the production of consumer goods, it turns out that these polymers are non-Newtonian in their behaviour: their viscosity is not constant. In particular, it is commonly observed for many polymers that the shear viscosity decreases by orders of magnitude with increasing deformation rate $\dot{\gamma}$. Accounting for this nonlinearity in the properties of filled polymers is an important albeit challenging task with direct application in the polymer industry, since polymers are often filled with particles to change their properties. The reasons for filling polymers with rigid particles are multifold. The most common reasons are the improvement of mechanical properties of the end product, especially the enhancement of stiffness; the inhibition of flammability (natural and synthetic clays) and rendering of the electric conductivity (carbon black, carbon nanotubes) to otherwise non-conducting polymers.

In the present report we investigate the influence of the non-linear behaviour of the polymer matrix on the suspension viscosity by performing computational fluid dynamics (CFD) simulations [1]. We specifically simulate the flow of a Bird-Carreau fluid around a spherical particle and compute the effective viscosity of the suspension. The Bird-Carreau model used in the simulations captures the non-linear viscosity of a polymer melt very well. At low rates of deformation the polymer viscosity exhibits a Newtonian plateau with a constant viscosity η_0. After a crossover regime, that appears around deformation rates of the inverse of the longest relaxation time λ, the

polymer viscosity follows a power-law with the slope n at high rates of deformation. Using the results of the simulations we have been able to propose a modification of the original Bird-Carreau model [1] to account for the presence of rigid spherical particles in the dilute limit:

$$\eta^*(\dot{\gamma}) = X(\varphi)\eta_0[1 + (a_d(\varphi,n)\lambda\dot{\gamma})^2]^{\frac{n}{2}}$$

Here X is the hydrodynamic amplification factor that shifts the Newtonian plateau to higher viscosity values and a_d is the strain amplification factor that shifts the crossover regime to lower deformation rates. We originally introduced the strain amplification factor a_d in an earlier work [2], using an analytical estimate for its value. Now we derive the hydrodynamic and strain amplification factors from the CFD simulations of dilute suspensions. As polymers are normally filled with relatively high concentrations of particles, we extend our model to higher volume fractions of particles using a mean field approach. For this we introduce a free parameter φ_{max} into the expressions for amplification factors X and a_d. This parameter defines the crossover between a fluid behaviour and a paste-like behaviour of the suspension: as φ approaches φ_{max} the suspension starts to exhibit a yield stress. Fig. 1 shows the comparison of the modified Bird-Carreau model with data for a thermoplastic melt filled with micrometre sized glass beads by Poslinski et al. [3]. For this the Bird-Carreau model is fitted first to the data set with $\varphi = 0\%$ to extract the parameters of the unfilled system. The free parameter $\varphi_{max} = 38\%$ has been estimated from the increase of viscosity in the linear regime at small deformation rates. As can be seen from Fig. 1 the predictions of the modified Bird-Carreau model are rather good. Especially the shift of the crossover between the linear and non-linear behaviour is captured very well.

Fig. 1:
Predictions of the modified Bird-Carreau model for a polymer melt filled with glass beads. The data is taken from Poslinski et al. [3].

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[1] J. Domurath, M. Saphiannikova, J. Férec, G. Ausias, G. Heinrich. Journal of Non-Newtonian Fluid Mechanics. 221 (2015) 95–102.
[2] J. Domurath, M. Saphiannikova, G. Ausias, G. Heinrich. Journal of Non-Newtonian Fluid Mechanics. 171–172 (2012) 8–16.
[3] A. J. Poslinski, M. E. Ryan, R. K. Gupta, S. G. Seshadri, F. J. Frechette. Journal of Rheology. 32 (1988) 703–735.

Model simulations on network formation and swelling as obtained from cross-linking co-polymerization reactions

Michael Lang, Andreas John,
Jens-Uwe Sommer

Superabsorbent materials combine the properties of soft rubber networks with the large osmotic pressure of strong poly-electrolytes to achieve materials that can absorb up to 1000g water or about 100g dilute salt solution per gram of material and retain it under moderate pressure [1]. These materials are typically synthesized using free-radical chain polymerization in aqueous acrylic acid solution in the presence of cross-linkers. This allows to adjust the material properties by a simple modification of the composition of the reaction bath. The vast majority of these products is used in diapers or other sanitary products [2], while further applications can be found in quite diverse fields ranging from horticultural water retention agents [3] to water penetration blockers in underground power or communication cables [4].

The principles of cross-linking co-polymerization in solution were studied in the presence of di-, tri- or tetra-functional cross-linkers using the Bond Fluctuation Model (BFM) [5]. Network formation was analyzed for varying cross-linker reaction rates, cross-linker composition and number fraction, cross-linker functionality and time dependent initiator release. Additionally, the effect of inhomogeneous radical release and radical aging was examined. For all simulations we observe an auto-acceleration of reaction kinetics similar to the 'Trommsdorff-Norrish effect' (or 'gel effect') independent of the degree of cross-linking, see Fig. 1. The interesting point of our results in comparison with several attempts to explain this effect [6, 7] is that neither temperature increase nor viscosity changes (only minor changes in the mobility of free monomers as function of conversion) nor hydrodynamics play an important role in our simulations. This result helps to sort out some of the large number of previously discussed models on this effect, [6, 7].

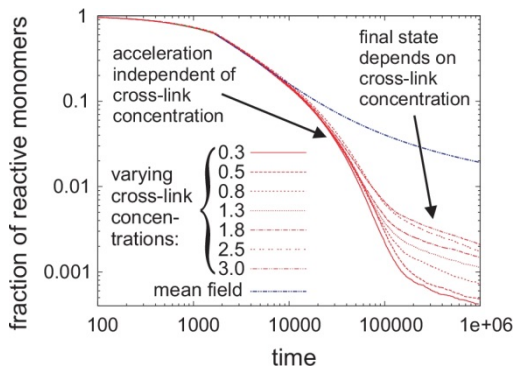# Polymere Netzwerke: Struktur, Theorie und Anwendung

Fig. 1:
Reaction kinetics is independent of cross-link content except of the very late time regime.

Interestingly, while kinetics does not follow mean field models, the resulting structure can still be described using mean field concepts. In particular, the weight distribution of "chains" that result from reactions of one radical and the number distribution of cross-linkable sites on these chains are approximated by Poisson distributions. Delayed release of initiators causes a pronounced broadening of these distributions that can be modeled by a partitioning of the reaction bath into compartments with different initiator density and instant initiation.

As a first test of the performance of the simulated network structures as superabsorbent materials, the a-thermal swelling of neutralized networks was analyzed by computer simulations. In order to obtain a qualitative match of the equilibrium swelling data with the prediction of the Flory Rehner model [8], we had to consider the weight fraction of elastically active material, ω, the weight fraction of the gel, ω_{gel}, and the contributions of entanglements to modulus, which is expressed by using an effective degree of polymerization N_{eff}., see Fig. 2.
With our work, we could relate these three parameters to the reaction conditions for network preparation. Thus, our results allow for a direct relation between of material properties to network structure, which is essential for a tailor made design and optimization of material properties.
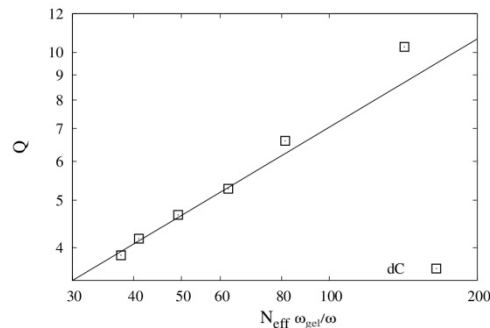

Sponsor and Co-operation:
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[1] F. L. Buchholz, A. T. Graham. Wiley-VCH, New York, Chichester, Weinheim, Brisbane, Singapore, Toronto, (1998).
[2] R. Harrer, Chem. Unserer Zeit, 48 (2104) 230.
[3] K. M. Raju, M. P. Raju, Polym. Int. 50 (2001) 946.
[4] J. Houben, W. Krug, US Patent US 6043311 A.
[5] M. Lang, A. John, J.-U. Sommer, Polymer 82 (2016) 138-155.
[6] C. Barner-Kowollik, G. T. Russell, Prog. Polym. Sci. 34 (2009) 1211.
[7] D. S. Achilias, Macromol. Theory Simul. 16 (2007) 319.
[8] P. J. Flory, J. Rehner Jr., J. Chem. Phys. 11 (1943) 521.

Fig. 2:
Equilibrium degree of swelling, Q, as function of the effective degree of polymerization, N_{eff}, that models the elasticity of the network, the weight fraction of elastically active material, ω, and the weight fraction of the gel, ω_{gel}. The line indicates a power law with a power of 0.6 that agrees within error bars with the theoretical prediction of Flory and Rehner [8].

Polymere Netzwerke: Struktur, Theorie und Anwendung

Fig.1:

Molecular bottlebrush (top) consisting of a backbone with (red beads) densely grafted side chains (blue beads) as a building block of polymeric material (bottom).
D denotes bottlebrush diameter (thickness) and l_p is persistence length of backbone. Both quantities are proportional to the square-root of the degree of polymerization of side chains N.

The dense state of polymer bottlebrushes

Jaroslaw Paturej

Bottlebrushes are huge macromolecules synthesized in a precise fashion by grafting side chains to a linear backbone using atom transfer ("living") polymerization technique. The physical properties of bottlebrushes are very distinct from conventional linear polymers. Densely grafted side chains not only expand thickness of polymer chains (Fig. 1) but also allow to control their stiffness.

Molecular dynamics simulations and scaling theory give evidence that bottlebrushes in a melt state behave as liquid-like filaments. Persistence length l_p of solid-like filaments raises markedly with diameter D ($l_p \propto D^4$) which results in an increase of entanglements, ordering (nematic) transitions and introduces anisotropy to mechanical properties of bulk polymers. By contrast, bottlebrushes in a melt remain flexible with growing diameter D since their persistence length behaves as $l_p \propto D \propto N^{1/2}$ [1] where N is the degree of polymerization of side chains (Fig. 1). The adjustable interplay between bottelbrush diameter and stiffness allows to synthetize novel polymer materials with superior mechanical properties.
The presence of entanglements is the major factor limiting mechanical properties of polymeric materials. To disentangle molecules

and fabricate soft materials, solvent species are usually added in order to swell polymer network and to obtain gels (Fig. 2).
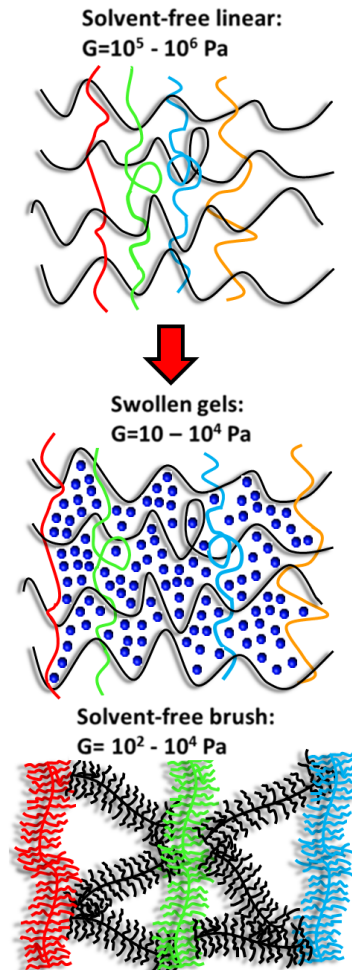

Fig. 2:
By changing architecture from linear chains to inherently strained bottlebrushes, polymeric material demonstrate significant decrease of modulus approaching that of swollen gels.

The drawback of gels is that solvent fraction can lead to phase separation, evaporation or leakage on deformation diminishing gel elasticity. The specific architecture of bottelbrushes promotes reduction of molecular overlap, screens backbones from entanglements and makes possible to tailor dry gels without the complications associated with a swollen (wet) gel. Dry gels posses unprecedented combination of low modulus ($\approx$ 100 Pa), high strain at break ($\approx$ 1000%) and extraordinary elasticity [2]. Similarly to solvent fraction

in wet gels, side chains of bottlebrushes act as swelling agent which decreases entanglement density in a polymer network. Contrary to solvent molecules, side chains are covalently attached to backbones and thus provide stability against deformation and temperature. The most striking feature of dry gels is that their mechanical properties can be systematically changed with bottlebrush diameter D [2]. The theoretically predicted elastic modulus G decreases with degree of polymerization of side chains as $G \propto D^3/l_p^6 \propto N^{-3/2}$ [1] and demonstrates excellent agreement with experimentally obtained results [2] (Fig. 3).
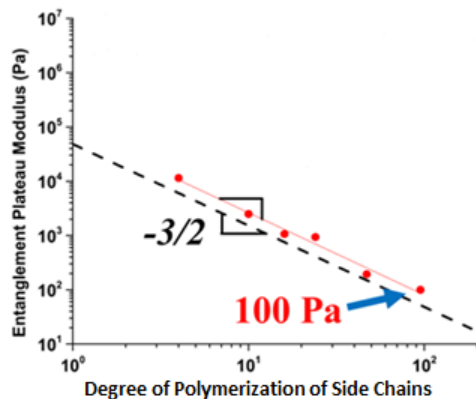

Fig. 3:
Experimentally obtained entanglement plateau modulus G (red circles) of bottlbrush melts plotted as a function of side chains degree of polymerization. Dashed line represents theoretically obtained power law $G \propto N^{-3/2}$.

The architectural control of elastic modulus has reduced the limit for softness present in conventional dry polymeric materials (rubbers) by a factor of 1000. Bottlebrush based materials also exhibit uniaxial compressive deformability of up to nine times. These attributes make them attractive alternatives for numerous applications including biocompatible implants that are able to closely mimic modulus of human tissue, scaffolds for tissue growth or as protective surfaces preventing accumulation of bacteria and fouling.

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[1]   J. Paturej, S. Sheiko, S. Panyukov, M. Rubinstein, Science Advances 2 e1601478 (2016).
[2]   W. Daniel, J. Burdyńska, M. Vatankhah-Varnoosfaderani, K. Matyjaszewski, J. Paturej, M. Rubinstein, A. Dobrynin, S. Sheiko, Nature Materials 15 183 (2016).