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.

Besonders interessant ist die Kombination von Vernetzung mit anderen Eigenschaften weicher Materialien, wie die Antwort auf äußere Stimuli oder die starke Adhesion von Polymerketten, hervorgerufen durch ionische Assoziation. Durch die Vernetzung von Polymeren, die Azobezen-Gruppen enthalten, können elastische Eigenschaften durch Licht beeinflusst werden. Wenn in einem Netzwerk neben den Chromophoren auch eine flüssig-kristalline Komponente enthalten ist, kann ein Phasenübergang durch Lichteinstrahlung induziert werden, welcher zu spontaner Deformation des Elastomers führt. Selbstheilung ist eine Eigenschaft lebender Systeme. Die hohe Durchdringung der Polymerketten in Kombination mit starken physikalischen Bindungen eröffnet die Möglichkeit selbstheilende synthetische Materialien zu erzeugen. In anwendungs-orientierten Arbeiten konnte gezeigt, dass insbesondere ionische Gruppen geeignet sind, selbstheilende Strukturen zu erzeugen, die Kräfte im Bereich praktischer Anwendungen standhalten. Polymere Netzwerke mit selbstheilenden Komponenten werden darüber hinaus in mehreren theoretischen Arbeiten untersucht. In dichten Polymersystemen, wie in Elastomeren, spielt die Anwendbarkeit der Gaußschen Elastizität - oft als Flory-Theorem bezeichnet - eine entscheidende Rolle für die theoretische Beschreibung. In einer kombinierten Theorie-Simulations-Studie konnte nun gezeigt werden, dass unter Berücksichtigung von Korrekturen zur Abschirmung des ausgeschlossenen Volumens eine Verallgemeinerung des Flory-Theorems gefunden werden kann, die in sehr guter Übereinstimmung mit experimentellen Daten und Simulationsergebnissen steht.

Bei der Synthese und Etablierung von bi-sensitiven interpenetrierenden Netzwerken als Sensoren und Aktoren in der Mikrosystem-technik konnte ein entscheidender Durchbruch erzielt werden. Hierzu wurden die Quellungs-kinetik im Detail untersucht und ein einfaches Modell zur Vorhersage unterschiedlicher Quellkinetiken von definierten Gelgrößen entwickelt. Für den Einsatz von chemischen Ventilen in der Mikrosystemtechnik wurden drüber hinaus tetra-sensitive Graftgele synthetisiert. Ihre iterative Schaltbarkeit konnte gegenüber pH- und Temperatur-änderungen sowie Salz- und Lösungsmittel-konzentrationen nachgewiesen.

Im anwendungsorientierten Bereich des ST3 wurden die Arbeiten auf dem Gebiet der funktionalen Elastomerwerkstoffe auf Basis vernetzter Kautschukpolymere konsequent weitergeführt und resultierten in einer Reihe erfolgreicher Projekteinwerbungen bei öffent-lichen Mittelgeber und der Industrie. Die international führende Rolle bei Entwicklung und Charakterisierung von Hochleistungs-elastomernanokompositen und „smarten" Elastomeren wurde weiter ausgebaut und wird durch die Nominierung von Dr. Amit Das für den renommierten Sparks-Thomas Award der Rubber Division der American Chemical Society unterstrichen. Besonders hervor-gehoben seien hier die Forschungsarbeiten zur Entwicklung selbstheilender Elastomere auf Basis kommerziell verfügbarer Kautschuke sowie zu zinkhaltigen Nitrilkautschuk-Elastomer-Nanokompositen. Die langjährigen wissenschaftlichen Verdienste von Prof. Gert Heinrich im Bereich von Kautschuk und Elastomeren erfuhren im vergangenen Jahr ihre internationale Würdigung durch drei hochrangige Preise: George Stafford Whitby Award der Rubber Division der American Chemical Society, Carl-Dietrich-Harries-Medaille der Deutschen Kautschuk-Gesell-schaft und Colwyn-Medaille des Institute of Materials, Minerals and Mining (IOM3), UK.

Self-healing elastomers based on ionic liquid modified bromo-butyl rubber

Amit Das, Aladdin Sallat, Frank Böhme, Marcus Suckow, Klaus Werner Stöckelhuber, Sven Wießner, Brigitte Voit, Gert Heinrich

In this work, we report on the development of an intrinsically self-healable technical rubber. The applied scientific approach may even pave the route to a new class of rubber materials of high mechanical performance without any conventional chemical crosslinks, i.e. those rubbers do not require the usual vulcanization process but behave like covalently crosslinked elastomers. Bromo-butyl rubber (bromine modified isoprene-isobutylene copolymer, BIIR) was mixed with 1-butyl imidazole using an internal mixer. During this mixing process the reactive allylic bromine groups of BIIR were converted into ionic imidazolium bromide groups which were able to form an ionic network. Mechanical and dynamic mechanical characterizations supported the crosslinked nature of the modified rubber.

Apart from the typical elastic behavior, the ionically crosslinked rubber exhibited unusual self-healing properties. Fig. 1 shows a schematic representation of the network formation by ionic association of the imidazolium bromide groups and of the assumed mechanism of self-healing. Scanning electron microscopic (SEM) studies on cut samples, which were allowed to heal some time, directly verified complete healing.

The self-healing nature of the modified BIIR was explored by stress-strain measurements (Fig 2). For this purpose cut samples were allowed to heal at different temperatures and for different times. It was observed that the healing effect was stronger at higher healing times and higher temperature.

The self-healing characteristics were directly reflected in the tear fatigue analysis of the modified rubber. The relation between a stable crack growth rate and the tearing energy follows the Paris-Erdogan power law (with exponent m) which is written as $(da/dn) = T^m$, where (da/dn) represents the crack growth rate and T is the tearing energy.

Fig. 3 shows the results of the tear fatigue analysis of the ionically modified BIIR in comparison to a sulfur cured BIIR. At any tearing energy, the crack growth rate of the modified BIIR is almost on order of magnitude lower compared to the sulfur cured rubber.
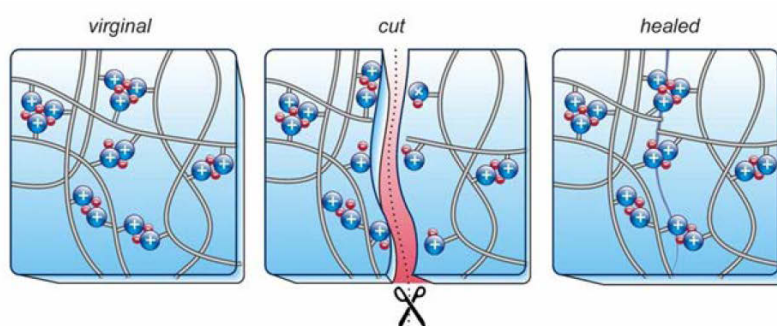
Fig. 1:

Schematic representation of the self-healing process by reformation of ionic associates in an ionic rubber network
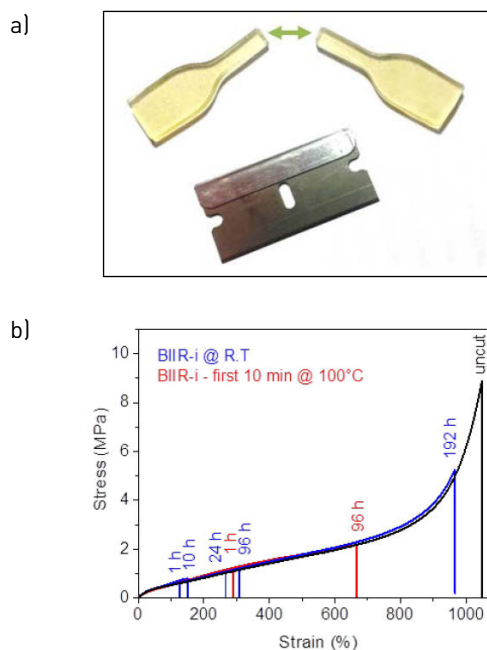
a)

b)

Fig. 2:
a) Cut tensile test specimen of the bromobutyl rubber (BIIR) modified by butyl imidazole,
b) Stress-strain plots of mended samples of the imidazolium-modified BIIR after 1 to 192 hours of healing at room temperature (blue). Some samples were maintained at 100 °C for the first 10 min of the total healing time (red). For comparison, the stress-strain plot of the uncut sample is shown (black).

Thus the modified BIIR exhibits a much higher resistance against tearing and consequently could show a much longer service life time of a dynamically loaded rubber part before ultimate failure occurs. We assume that due to the presence of ionic clusters in the modified BIIR the crack propagation rate is significantly lowered.

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The ionic clusters present in the crack tip are assumed to dissociate into smaller aggregates without being destroyed completely. Moreover, ion hopping during elongation may facilitate further re-aggregation or re-association of the ion pairs, leading to a higher crack resistance. A higher crack growth resistance is also known if the rubber is reinforced with fillers like carbon black or silica. With respect to the fracture mechanical properties, the imidazole-modified BIIR behaves like a filled rubber composite despite the absence of any reinforcing filler particles.

Fig. 3:
a) Set-up of the tear fatigue analyzer (TFA) for the determination of the crack growth rate,
b) Crack growth rate as a function of tearing energy. The imidazole-modified rubber (blue line) exhibits distinctly lower crack growth rates than the sulfur cross-linked one (red line). The numbers indicate the percentage of the deformation amplitude.

a)

b)
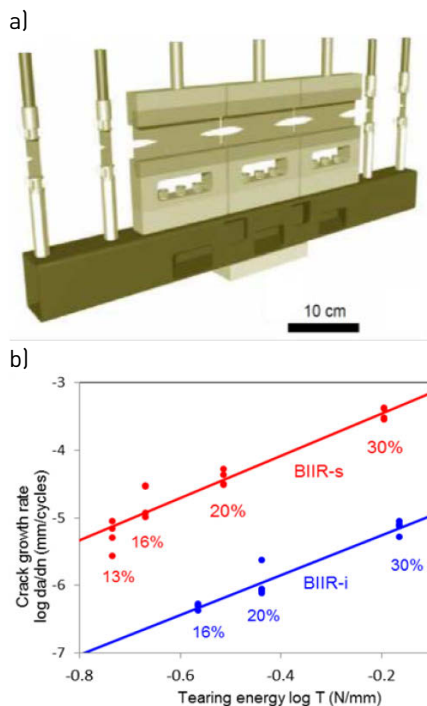
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Co-operation:
Prof. K. Saalwächter, Martin-Luther-Universität Halle-Wittenberg, Institut für Physik

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Enzymatic reactions with hydrogels in microfluidics: Integration, stability and reusability

David Simon, Toni Heroldt, Martin Peiter, Brigitte Voit, Dietmar Appelhans

Enzymes are one of the potential solutions to the question how to make synthetic chemistry green.[1] They react chemo-, stereo- and regio-selectively without any side reactions under adequate conditions (~37°C, no pressure).[2,3] To resist the harsh conditions of a continuous usage and to ensure the reusability, the enzymes can be immobilized in hydrogels. Those hydrogels have advantageous properties such as (I) mimicking the natural environment of the immobilized enzymes and (II) supporting the growth of different cell types. This is caused by the adaptable chemical and mechanical characteristics of hydrogel compositions.[4,5].

Hydrogel films or solutions can be easily structured by photolithography on solid substrates followed up on their integration in microfluidic channels to build up a microfluidic reactor. Crooks et al. presented a first microfluidic reactor at which enzymatic cascade reactions have been established.[6] But there is a lack of long-term stability and reusability of such a complex enzyme-loaded hydrogel system. This was the starting point for our own study in this research field.

Fig. 1 presents the setup of our established enzymatic microfluidic reactor. Enzyme-loaded hydrogel dots composed of poly(ethyleneglycol) diacrylate, 2-(dimethylamino)ethyl methacrylate, 2-hydroxyethyl methacrylate and lithium acylphosphinate,[7] used as a photoinitiator, were fabricated on glass substrates by a photo-lithography approach.

With this established setup a trienzymatic cascade reaction, containing lactase (Lac), glucose oxidase (GOx) and horseradish peroxidase (HRP), was simultaneously integrated in each hydrogel dot in the microfluidic reactor. Successful enzymatic cascade reaction was detected by the final conversion of UV/vis-active dye ABTS with H_2O_2 conversion catalyzed by HRP (spectrometric detection at wavelength of 405 nm). Surprisingly, immobilized trienzymatic cascade reaction is
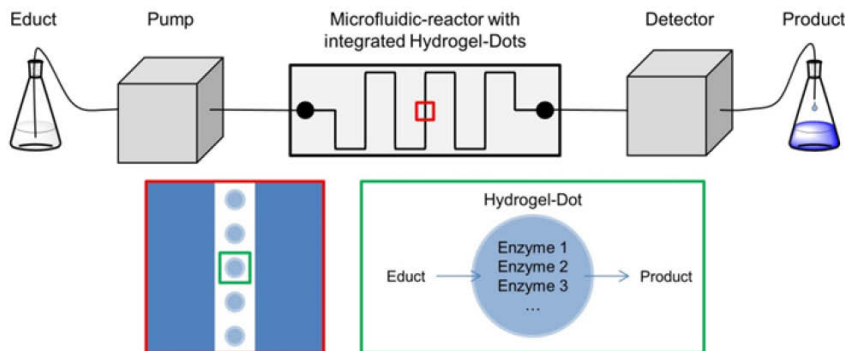
more active as found for the same trienzymatic cascade reaction in pure solution (Fig. 2). Concurrently, the long-term stability of this trienzymatic cascade reaction is still given after a storage time of 21 days (40 % of relative activity compared to the starting 100 % relative activity). One deciding key parameter for the trienzymatic cascade reaction is the successful consumption of H_2O_2 by HRP. When the H_2O_2 concentration is too high, then negative influence on the complete enzymatic cascade reaction can be observed by lowering the relative activity drastically. But if H_2O_2 is continuously produced and consumed during the cascade reaction, the stability of HRP is increased within the cascade reaction. Finally, the enzyme/hydrogel dots in microfluidic reactor (Fig. 1) are reusable and still have an activity of 40 % after 4 cycles of usage within every reactor test (test time of at least 15 hours for each cycle).

In summary, we demonstrated the establishment of a trienzymatic cascade reaction in a microfluidic reactor (Fig. 1) with the desired long-term stability and reusability. Consequently the next step will be (I) the establishment of another multienzymatic cascade reaction by using even more sensitive enzymes and (II) the integration of Raman technology for the direct measurement of reaction products.
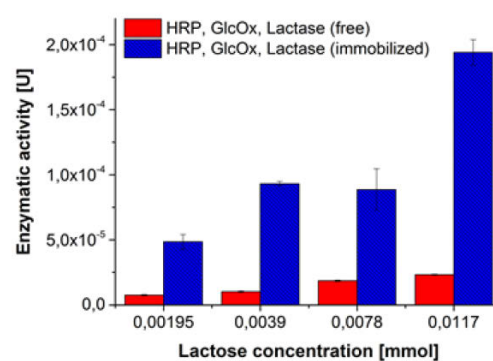
Co-operations:
S. Häfner, Prof. A. Richter, Technische Universität Dresden, Institut für Halbleiter- und Mikrosystemtechnik

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Light-induced deformation of liquid crystalline azobenzene-containing polymer networks

Vladimir Toshchevikov, Tatiana Petrova, Jaroslav Ilnytskyi, Marina Saphiannikova

Two-component polymer networks containing liquid crystalline (LC) mesogens and azobenzene chromophores belong to a class of field-controllable smart materials which are able to change their shape under light illumination. Since the deformation driven by light can be controlled rapidly and precisely, these materials have a great potential as a working component in light-controllable sensors, actuators, micropumps, artificial muscles. In the present report we focus on the theoretical study of the light-induced deformation in azobenzene-containing LC polymer networks [1-3]. A statistical network model is proposed (Fig. 1), in which the mesogens of the LC network (green rods) are attached chemically to the network strands and the chromophores (orange ellipsoids) are either attached chemically or dispersed in the network.
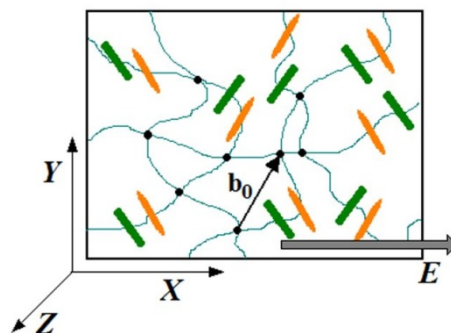

Fig. 1:
Model of a two-component polymer system consisting of the LC network with included azobenzene chromophores.

Under light illumination, the chromophores demonstrate cyclic trans-cis-trans photo-isomerization that leads to their preferable reorientation perpendicular to the polarization vector of the light E. The light-induced reorientation of chromophores is described by an effective orientation potential acting on each chromophore:

$$V = V_0 \cos^2 \theta \qquad (1)$$

Here θ is the angle between the long axis of the chromophore with respect to the light polarization E and V_0 is the strength of the orientation potential, which is proportional to the light intensity [1-4]. The computer simulations study of the kinetics of trans-cis-trans photo-isomerization has shown [5] that the light-induced reorientation of chromophores can be well approximated by the potential (1).
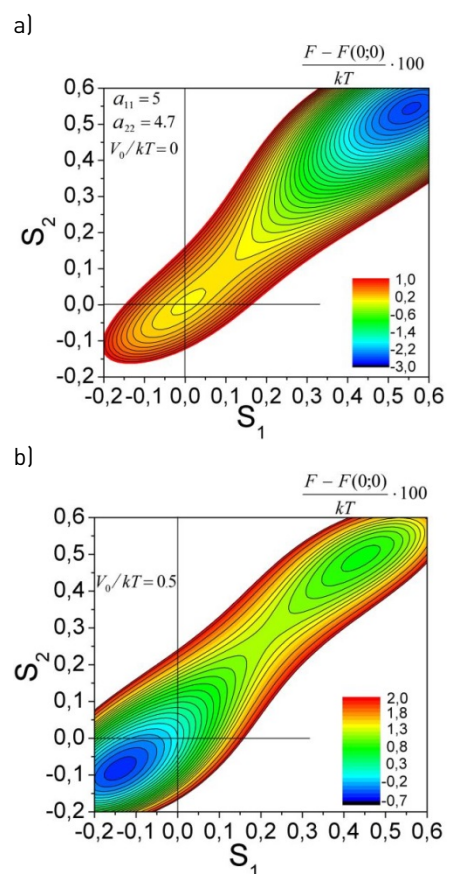
a)

b)

Fig. 2:
Free energy as a function of the order parameters in the absence of light (a) and under light illumination (b) at strong LC interactions. The volume fraction of chromophores is equal to 0.2.

Light-induced ordering of chromophores changes the energy of orientation interactions between the chromophores and mesogens. The free energy of these interactions can be expressed in terms of the mean-field approximation for uniaxial nematic mixtures [2,3]. The order parameters S_1 and S_2 for the chromophores and mesogens, respectively, can be determined from the minima of the free

energy. At strong LC interactions in the absence of light, $V_0 = 0$, the global minimum of the free energy takes place at $S_{1,2} > 0$ (Fig. 2a). This means that mesogens and chromophores are preferably oriented along a LC-director. Light illumination with the polarization direction E parallel to the LC director disturbs the initial LC state [6]. Above some threshold illumination, the global minimum of the free energy takes place at $S_{1,2} < 0$ and the network is transformed stepwise into a new LC state with preferable orientation of chromophores and mesogens perpendicular to the vector E. The light-induced reorientation of chromophores and mesogens leads to the light-induced deformation of the polymer network. Fig. 3 shows the elongation ratio λ as a function the strength of the potential V_0. One can see that the polymer network can demonstrate either contraction ($\lambda < 1$) or expansion ($\lambda > 1$) with respect to the polarization vector E, depending on whether the orientation of chromophores and mesogens is parallel (squares) or perpendicular (circles) to the backbones. The polymer networks with chromophores attached chemically to the network strands (filled symbols) are characterized by higher magnitude of deformation as compared to the networks with chromophores dispersed in the structure (open symbols).
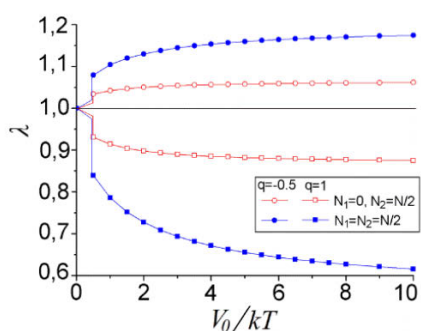

Fig. 3:

Elongation ratio λ as a function of V_0 for the networks with strong LC interactions. The volume fraction of chromophores is equal to 0.5.

The light-induced deformation of azobenzene-containing polymer networks depending on their structure was analysed in detail in [1-3]. It was shown that depending on the parameters of LC interactions an additional order in the plane perpendicular to the polarization vector

E can appear and the system becomes biaxial, with two axes being related to the vector E and to a preferable alignment of the chromophores in the plane perpendicular to E [1]. The biaxial order in azobenzene-containing LC polymers has been observed in many experiments presented in the literature. The structure-property relationships found in our theoretical work can be useful in future for further practical development of these light-controllable smart materials.

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Plastic yielding contribution to fracture toughness of polymers modified with rubber and inorganic fillers

Bernd Lauke

An effective way to improve toughness and at the same time stiffness and strength is to incorporate inorganic fillers together with rubber particles into brittle type polymers, see Garg and Mai [1] and Kinloch et al. [2]. Crack tip blunting and crack bowing (pinning) as well as rubber cavitation and localized plastic shear yielding were found to be responsible for the increase of toughness.The bonding strength between particles and matrix in common composites is usually reached before matrix yielding occurs. However, when there exists a high bonding quality at the particle/matrix interface, yielding around particles may be initiated first. Especially in hybrid composites consisting of nanosize rubber particles and microsize inorganic particles, there might be a special failure mechanism possible: Within the stress field of a crack the rubber particles may cavitate or debond from the matrix or even small (nanosize) inorganic particles may debond from the matrix before the microsize particles debond. Consequently the crack is propagating around the large particles within the filled matrix. Evidences to such behaviour were given by Han and Cho [3]. The present paper models a similar hybrid composite. A hybrid composite consisting of a brittle polymer matrix such as thermoset or poly-carbonate matrix, and two filler components which are very different in diameter are considered. The larger particles are enclosed in a material consisting of neat matrix and the nanoparticles which form an effective material, cf. Fig. 1.
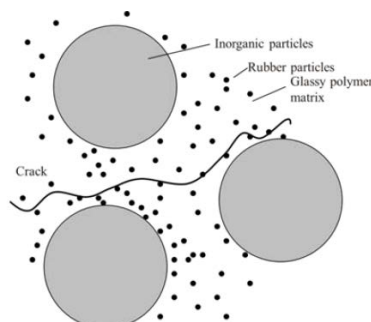
Now the local situation around one of the spherical microparticle within a spherical volume of the effective matrix material of radius, r_o, is considered in detail. This composite element placed at the position ρ, φ, z in front of the crack posses a local particle volume fraction of $\tilde{v} = (r_p / r_0)^3$. The radius, r_o, describes the limit extension to ensure that the stress field of one large particle does not interact with other large particles. At the outer surface, $r=r_o$, this volume element was loaded with the hydrostatic stress, σ_0. While loading such a composite element yielding begins at the radius where the yield condition is first satisfied, which assumes in the simplest case that the maximum shear stress reaches a critical value. The Tresca yield condition was used:

$$\sigma_r^{my} - \sigma_\theta^{my} = \sigma_{my} \text{ with } \sigma_r^{my} > \sigma_\theta^{my} \text{ and}$$
$$\sigma_\theta^{my} = \sigma_\phi^{my} \qquad (1)$$

where the index "my" of the radial, hoop and circumferential stresses indicates the effective matrix yielding region and σ_{my} is the yield strength of the effective matrix material. As soon as the stress, σ_0, causes hoop and radial stresses within the matrix that fulfil this relation, matrix yielding may start. During loading of a fracture mechanical specimen, the rubber nanoparticles cavitate while the microparticles remain bonded to the matrix. After cavitation the regions between these particles start local yielding with necking, cf. Fig. 2.
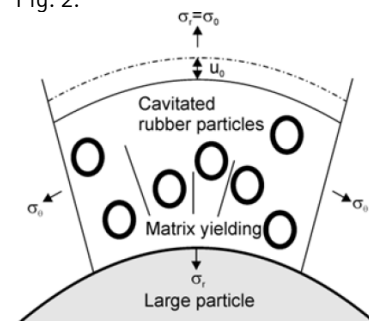
Fig. 2:
Volume segment near microsize particle under the action of hydrostatic stress, cavitated rubber particles cause plastic dilatation of the effective matrix.

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 as the integral over all local contributions:

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

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 hydrostatic stress, σ_0 : $\sigma_0(\rho) = \left(\beta R_c E_c / \rho\right)^{1/2}$ 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. (2) can be rewritten as:

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

with s_{min} and s_{max} as the minimum stress of yielding initiation and maximum stress respecively, more details are given in [4].

The yielding energy is derived by the product of applied force, F_0, with displacement, , at the matrix shell of radius, r_0:

$W_{my} = F_0 \Delta u = 4\pi r_0^2 \sigma_0 \Delta u$.

This displacement was calculated in [4] to be $\Delta u = r_0 \sigma_0 \Delta \widetilde{C}(s, \widetilde{v}, v_m) / E_m$ with the functionality given therein. With this value the yielding energy of the matrix shell around one debonded particle was calculated as:

$W_{my} = 4\pi r_0^3 (\sigma_{my} s)^2 \Delta \widetilde{C} / E_m$. The volume density of yielding energy is now given by:

$\eta_{my} = n_p\ W_{my} = \dfrac{3v}{4\pi r_p^3}\ W_{my} = \dfrac{3v}{E_m \widetilde{v}}\sigma_0^2\ \Delta \widetilde{C}$

With this knowledge, the crack resistance caused by matrix yielding follows from Eq. (3):

$$R_{dz} = R_{my} = \frac{12\beta R_c E_c}{E_m}\frac{v}{\widetilde{v}}\int_{s_{min}}^{s_{max}}\Delta\widetilde{C}(s)\,(s)^{-1}ds \qquad (4)$$

In the end, the composite crack resistance was derived by inserting Eq. (4) into Eq. (2) as:

$$\frac{R_c}{R_m} = \frac{v_m}{1 - \dfrac{12\beta E_c}{E_m}\dfrac{v}{\widetilde{v}}\displaystyle\int_{s_{min}}^{s_{max}}\Delta\widetilde{C}(s)\,(s)^{-1}ds} \qquad (5)$$

According to the functionality of the above integral the composite crack resistance depends on the elastic properties of components and the particle volume fraction. There is no dependence on particle size for the considered dissipation mechanism.

The proposed model was applied for a hybrid composite consisting of rubber filled epoxy and additionally filled with glass spheres which have the following material properties: elastic modulus E_p= 64 GPa and Poisson's ratio v_p = 0.2. The elastic properties of the epoxy matrix are given by: $E_{m,0}$= 3 GPa, $v_{m,0}$= 0.35. The result of crack resistance for the above given material properties is shown in Fig. 3. The solution of two different values of the parameter β which determines the size and shape of the yielding zone, ρ_y, are compared. Composite crack resistance increases at first with increasing microparticle content, v, and then reaches a plateau and for higher values starts to decrease again. Such behaviour was measured for epoxy ternary composites filled with glass beads and rubber particles by Kinloch et al. [2]. The new and interesting point is that the model is able to describe such a variation with v.

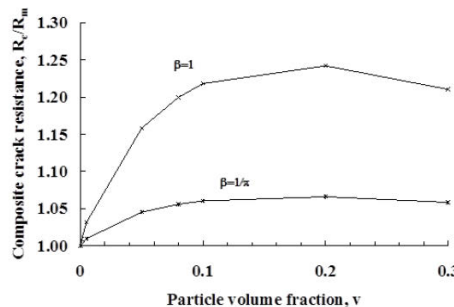# Polymere Netzwerke: Struktur, Theorie und Anwendung

Fig. 3:

Normalized composite crack resistance (fracture toughness) as a function of microparticle volume fraction, displaying the influence of matrix yielding; influence of the shape factor, β .

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Verallgemeinerung des Flory-Theorems für die Konformationen einzelner langer Polymerketten in einer Schmelze aus kurzen Ketten

Michael Lang, Jens-Uwe Sommer

Eines der grundlegenden Konzepte, um die Konformationen von Makromolekülen zu verstehen, ist das ausgeschlossene Volumen, mit dem die effektiven Wechselwirkungen zwischen einzelnen Monomeren eines Makromoleküls beschrieben werden. Bereits von Paul Flory wurde zu Beginn der 50er Jahre gezeigt [1], dass dieses ausgeschlossene Volumen in einer Schmelze aus Polymeren proportional zum inversen Polymerisationsgrad der Polymere in der Schmelze sein sollte, was zur Konsequenz hat, dass große lineare Polymere in einer monodispersen Schmelze in erster Näherung Konformationen besitzen, die äquivalent zu einem Zufallspfad sind. Dagegen sollte das gleiche Polymer in einer Schmelze aus Monomeren Konformationen wie in ein selbstvermeidender Pfad ('self-avoiding walk') annehmen und damit für hohe Polymerisationsgrade deutlich größer als in einer Schmelze sein. Obwohl bereits sehr früh experimentell nachgewiesen werden konnte, dass die beiden Grenzfälle in guter Näherung angenommen werden, konnte bis heute keine einzige Studie das postulierte Verhalten für den Übergangsbereich bestätigen [2]. Daher war das Konzept des ausgeschlossenen Volumens für eine Schmelze noch nicht in vollem Umfang experimentell belegt.

Mit Hilfe von Monte-Carlo-Simulationen wurde am IPF das Konformationsverhalten isolierter Makromoleküle mit Polymerisationsgrad N in einer Schmelze des gleichen Polymers mit verschiedenem Polymerisationsgrad P untersucht [2]. Dabei konnte zunächst wie in den experimentellen Arbeiten kein universelles Verhalten (alle Datenpunkte folgen einer einheitlichen Funktion im Skalenplot) für die räumliche Ausdehnung des großen Moleküls im Übergangsbereich $N/P^2 \approx 1$ gefunden werden (siehe Abb. 1).

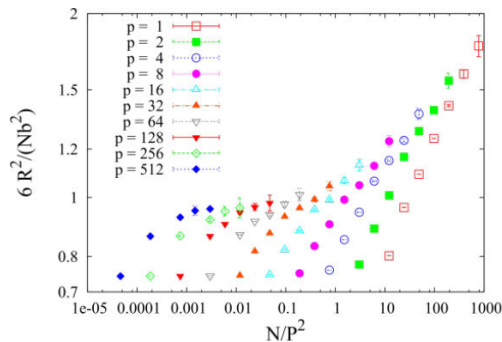# Polymere Netzwerke:
Struktur, Theorie und Anwendung

Abb. 1:

Mittlere quadratische Ausdehnung R^2 der Makromoleküle mit Polymerisationsgrad N normiert auf die quadratische Ausdehnung einer idealen Kette, $Nb^2/6$, als Funktion des Polymerisationsgrades der umgebenden Schmelze, P in universeller Darstellung als Funktion von N/P^2.

Computersimulationen besitzen jedoch gegen-
über dem Experiment den großen Vorteil, dass
weitere Details der Konformationen direkt
analysiert werden können. So konnte gezeigt
werden, dass in bi-dispersen Schmelzen auf
kurzen Skalen ähnliche Bindungskorrelationen
wie in einer mono-dispersen Schmelze [3]
vorliegen, was zu einer Renormierung der
Referenzgröße der großen Moleküle führt.
Darüber hinaus konnte gezeigt werden, dass
Kettenenden sich im Mittel besser an eine
benachbarte Kette packen, was zu einer
Renormierung des tatsächlichen ausgeschlos-
senen Volumens als Funktion von P führt.
Schließlich wurde noch mit den Simulations-
daten belegt, dass im Falle P>N keine
zusätzliche Kompression der Polymere mit
Polymerisationsgrad N erfolgt. Unter Berück-
sichtigung dieser Einflüsse ergibt sich in der
Tat ein universelles Verhalten für die Aus-
dehnung der Makromoleküle wie ursprünglich
von Flory postuliert und in Abb. 2 gezeigt. Mit
dieser Arbeit konnte daher nach 70 Jahren
schließlich eine wichtige Lücke in unserem
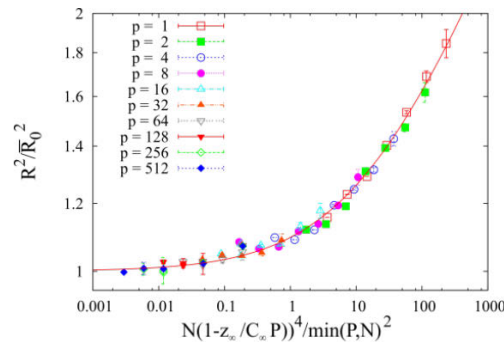Verständnis der Konformationen von Makro-
molekülen geschlossen werden.

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Carolina zu Chapel Hill, NC, USA

[1]   P. J. Flory: J. Chem. Phys. 10, 51-61 (1942)
       und J. Chem. Phys. 17, 303-310 (1949).
[2]   M. Lang, M. Rubinstein, J.-U. Sommer:
       ACS Macro Letters 4, 177-181 (2015).
[3]   J. P. Wittmer, P. Beckrich, H. Meyer,
       A. Cavallo, A. Johner, J. Baschnagel: J.
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Abb. 2:

Gleiche Daten wie Abb. 1. Die Auftragung berück-sichtigt jedoch die renor-mierte Referenzgröße der Ketten und die neu ermit-telten Korrekturen für das ausgeschlossene Volumen.