

Materials Research in the Group of Polymer Chemistry at ETH

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Abstract: The research activities of the group of Polymer Chemistry in the Department of Materials at ETH Zürich are briefly reviewed. The main research areas are concerned with (i) the behavior of polymeric solids, (ii) polymers and inorganic materials, and (iii) multi-functional polymeric materials. All three themes involve modeling, but the first one has a particularly strong simulation component. Two Zürich start-up companies have emerged from the group, Global Surface AG and MatSim GmbH.

Keywords: Macromolecules · Materials · Modeling · Polymers · Synthesis

Introduction

Polymeric materials and polymer-based materials systems have gained a large share of the structural and functional materials market. The trends point to ever more complex and more miniaturized systems based on multi-functional materials. We develop polymers and polymer-based materials that fulfill these needs as well as modeling methodologies to support the approach. To this end, we collaborate with partners in the Institute of Polymers, in the Department of Materials, inside ETH, and in Swiss and international Technical Colleges, Universities, and industrial research and development laboratories. Our main strengths are the breadth of our interest and expertise, and the tight and harmonious combination of modeling with experiment. Our goals are to conduct research of the highest quality on subjects of scientific relevance and industrial interest, and to educate and train materials engineers and chemists for leadership in science and technology.

In addition to the extensive experimental facilities of the Institute of Polymers, the group maintains a significant

park of state-of-the-art equipment for more specialized use. Together with the combined facilities available in the Institute of Polymers and the Department of Materials as well as the Department of Chemistry, practically all tasks in synthesis, characterization, processing, and testing of polymeric materials can be carried out efficiently and safely.

The group of Polymer Chemistry has three major research areas: the behavior of polymeric solids, polymers and inorganic materials, and multi-functional polymeric materials. All three themes involve modeling, but the first one has a particularly strong simulation component.

The Behavior of Polymeric Solids

The Structure of Polymers and Heterogeneous Materials at the Molecular Level

The rational design of materials is based on the relationships between structure and properties. Therefore, the development and the improvement of polymeric and composite materials with specific properties require a detailed understanding of their structure. While the chemical structure of polymers and composites can be rather easily characterized, the conformation and the packing of glassy or rubbery polymers and heterogeneous materials often elude precise description. The difficulty roots mainly in the absence of long range order. This absence greatly handicaps scattering techniques, otherwise successfully used to

study the structure of crystalline compounds.

In the last years, solid-state Nuclear Magnetic Resonance (NMR) has become a very useful tool to characterize complex systems. In collaboration with the group of Prof. Beat Meier at the Laboratory of Physical Chemistry of ETH, we are developing and applying solid-state NMR techniques to study disordered systems. These techniques can measure specific structural parameters, such as dihedral angles, interatomic distances, and relative orientations of nearest-neighbor molecular fragments, even if these parameters are widely distributed.

Besides the development of new experimental schemes, the research focuses on three topics. First, we study the detailed conformation and packing of polymer chains. These experimental results are of primary importance to understand the onset of crystallization of glassy polymers and to be able to generate realistic computer simulations of glassy polymers at the atomistic level (*e.g.* Fig. 1). Second, we investigate the structural changes after plastic deformation of polymers in order to clarify the mechanisms of this process. Third, in collaboration with the group of Prof. Paul Smith and Dr. Wanda Andreoni of the IBM Research Laboratory Zurich, an effort is made to characterize the structure of heterogeneous materials, especially multi-phase and supramolecular systems with highly anisotropic properties (Fig. 2). The optimization of these systems for technological applications is achieved by identifying and tailoring the relevant structural features.

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The Behavior of Heterogeneous Materials

Advanced multi-phase composite materials are indispensable today in many demanding applications. These materials combine the best properties of two or more single-phase, homogeneous materials and often exhibit a unique portfolio of technologically important properties. Most current multi-phase materials have a random microstructure with inclusions of different sizes and shapes forming an enormous variety of local microstructural configurations. The limits within which the overall effective properties can vary are specified by rigorous upper and lower variational bounds; however, for many multi-phase materials these bounds give impractically wide estimates so that the question arises, which morphologies can actually realize the extremes predicted by the bounds. We take a numerical approach for identifying these morphologies. Monte Carlo simulations are used to generate representative multi-inclusion models of actual random composite materials. The composite microstructure is reproduced by periodic meshes of several million (or more) non-overlapping tetrahedra that cover the space inside a disordered unit cell without holes. Variational formulations are used to construct the total energy of these periodic models in the presence of external thermomechanical, electric, and other fields. Assuming realistic phase properties, a displacement-based finite element method is employed for finding the overall responses as well as the underlying local fields in the constituents (see also Fig. 3).

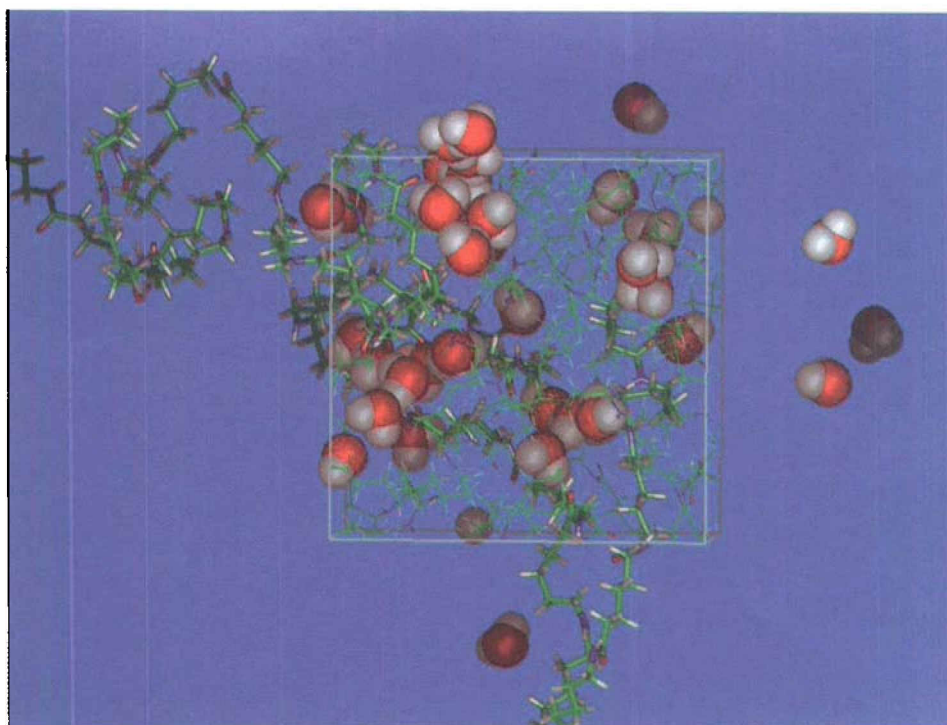


Fig. 1. Small molecules dissolve in polymers; this can be understood accurately and estimated by molecular-modeling methods. Here, the chemical potential of water in amorphous Polyamid-6 is calculated at a concentration of 10 wt-% (corresponds to 6 wt-% in the common semi-crystalline material), 1 bar, and 300 K. The system is modeled with periodic boundary conditions – the polymer is drawn as ball-and-stick model, its images, which fill space completely, are shown in the box as light copies, and the water molecules are drawn as space-filling models.

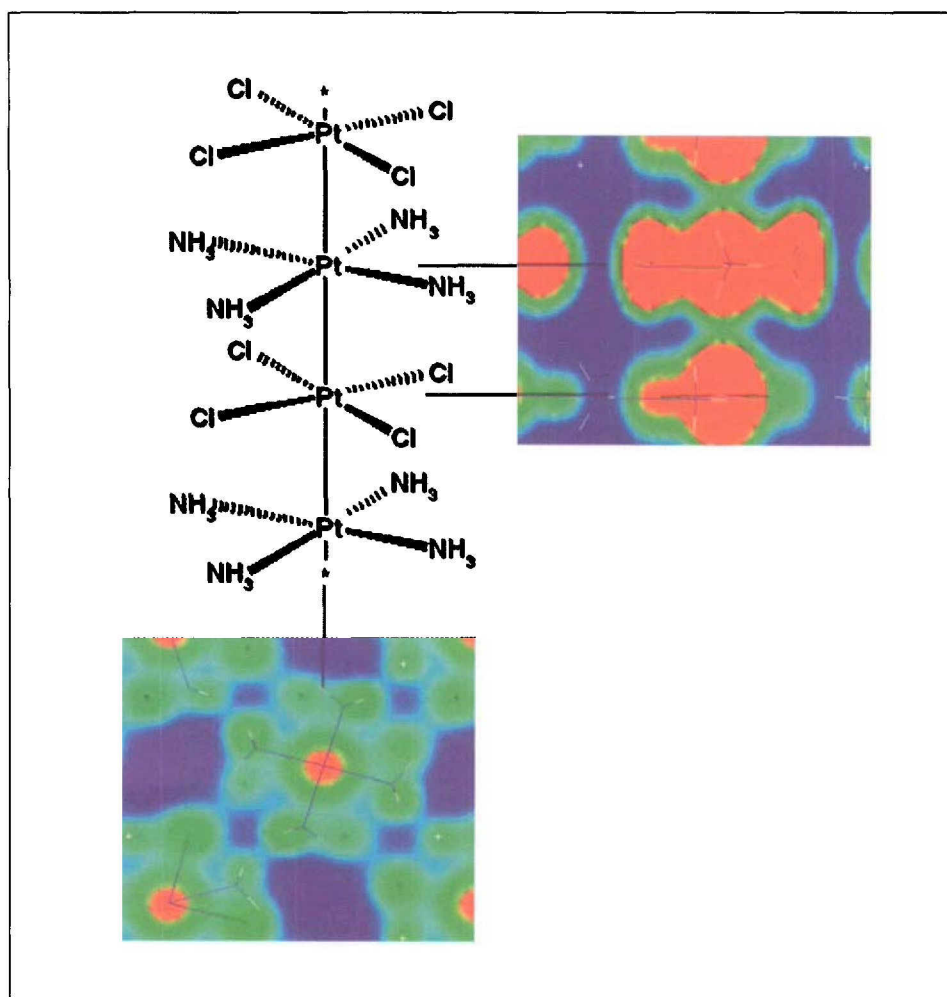


Fig. 2. Magnus salts are polymers with platinum main chain. In collaboration with the groups of Prof. Paul Smith and Dr. Wanda Andreoni (Zürich IBM Research Lab), polymers of this type are investigated. The theoretical electron density of Magnus' green salt, computed with density-functional theory, is displayed for the structure after Carr-Parrinello molecular-dynamics optimization. Top: side view of the platinum chains in a plane through the platinum atoms (the chains run top to bottom); color range is from 0 (dark blue) to 0.05 atomic units (red). Bottom: top view in a plane perpendicular to the platinum chains and midway between platinum atoms; color range is from 0 (dark blue) to 0.02 atomic units (red).

The computational efficiency and technological significance of the numerical approach taken shall be illustrated with on-going collaborative efforts; they include the matching of the thermal expansion coefficients of polymer-based composites for automobile applications and steels, the study of stiffening effects in carbon black and silica filled rubbers, the prediction of the overall stiffness of polymers reinforced by high-aspect ratio carbon nanotubes and cellulose whiskers, the understanding of the dielectric and optical properties of polymer-based materials for liquid-crystal displays, the use of carbon molecular sieves for the separation of oxygen and nitrogen, and others.

Multi-functional Polymeric Materials

Degradable Medical Implant Materials

Medical implant applications require materials with spectra of properties that differ for each case: the mechanical properties, for instance, should conform to those of natural tissue with different moduli and different finite-deformation compliances; depending on the particular situation, the surface behavior might have to match certain requirements of hydrophobicity in order for certain cells to attach or not attach to the implant; and the implant might have to carry specific groups to convey a given chemical or biological function. Degradability is often desired so that secondary operations to remove the implant can be avoided or in tissue-engineering applications, and the interval during which the implant sustains its initial properties as well as the time when all of the degrading material is resorbed or excreted are design criteria. We have developed a new class of biopolymers for use as scaffolds for tissue engineering as well as for implantable medical devices. These polymers are multi-block-copolyesters made from phase-incompatible telechelic polymers that form crystalline domains and amorphous, 'liquid' domains and satisfy all requirements stated above. The chemical names are rather impractical and the polymers have, therefore, been collectively trade-named 'DegraPol'.

The DegraPol polymers all have thermal processing temperatures (melting points) of *ca.* 130 °C and are melt processable and soluble in benign solvents. The glass transition temperatures of the polymers lie below 0 °C and the mechanical behavior in the range of highest interest, between refrigerator and body tem-

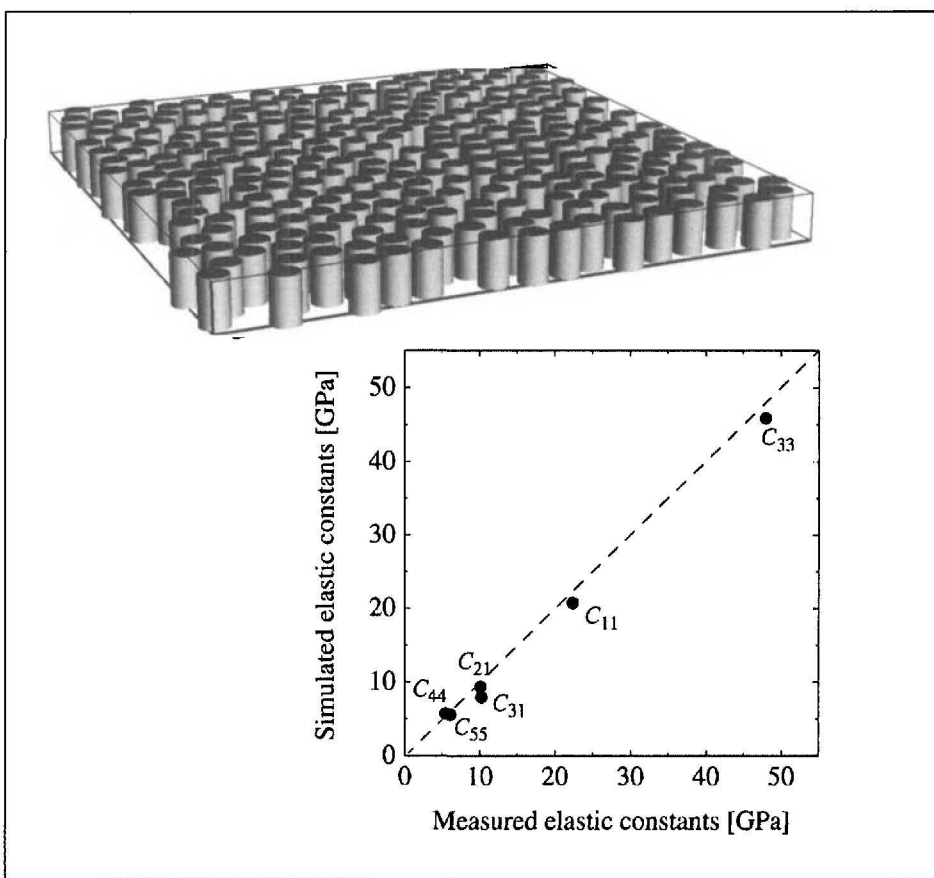


Fig. 3. A 'cell' with 289 infinitely long fibers of identical diameter, uniaxially oriented but randomly arranged in the plane perpendicular to the fiber axes. The material extends to infinity in all directions through the application of periodic boundary conditions. This structure is the basis for calculations with the displacement-based finite element method that finds the overall responses of the uniaxial composite to external and internal stimuli as well as the underlying local fields in the constituents. The simulation of all elastic constants of uniaxial composites yields results as accurate as experiment! Computations such as these can be performed with commercial software (Palmyra by MatSim GmbH, <http://www.matsim.com/>).

perature, is effectively invariant. Independent of the softening temperatures, the modulus of the polymer can be adjusted *via* the content of crystallizable blocks, between a few MPa up to almost 1 GPa. Parallel to the moduli, the strain at break varies from many hundred percents (these are biocompatible thermoplastic elastomers) down to a few percent for the hardest materials. The degradation behavior can be largely controlled *via* the structure of the 'soft' segment, *i.e.* the constitution of the block that makes up the amorphous domain, and the control of the microstructure of the 'soft' segment provides the possibility to create materials that lose their initial characteristics in a few days or in years, or anywhere in between. The degradation time is continuously adjustable.

It has been possible to find formulations of soft elastomer variations of DegraPol that disappear in nerve conduit applications to a very large extent within

a few months and practically completely within a year. A particular success was the fact that conditions could be found under which porous open-cell foams of DegraPol could be produced with adjustable cell sizes in the order of dozens to hundreds of micrometers and as pieces of dimensions of several centimeters (see also Fig. 4). These foams still retain the elastomeric behavior of the parent polymer and provide tissue-engineering objects that are tissue compatible and mechanically resilient.

High-temperature Resistant Functional Polymers

Most polymers start to fail in long-term applications at temperatures above *ca.* 150 °C. Together with Dr. Nicola Tirelli of Prof. Jeffrey A. Hubbell's group, we synthesized a class of more temperature-resilient polymers, polyquinolines, that exhibit glass temperatures of

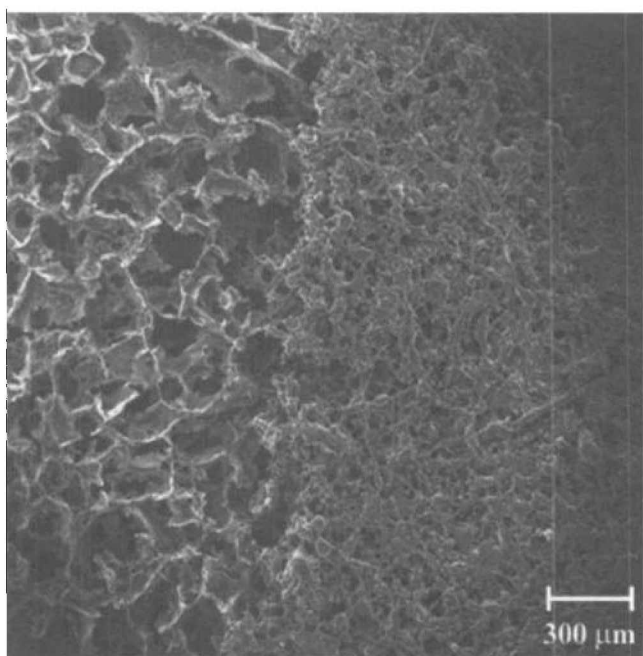


Fig. 4. Porous open-cell foams of DegraPol® can be produced with adjustable cell sizes in the order of dozens to hundreds of micrometers and as pieces of large dimensions. These foams still retain the elastomeric behavior of the parent polymer and provide tissue-engineering objects that are tissue compatible and mechanically resilient. The picture shows a transition electron micrograph (TEM) of a foam where in one object, pores with different pore sizes are joined through an abrupt transition region, without 'skin' between the regions.

ca. 300 °C and onsets of thermal degradation at ca. 550 °C (for an example, see Fig. 5). These polymers can be functionalized and we aim at imbuing them with unusual optical functionality: organic materials have potentially high performance characteristics as materials with unusual electromagnetic functionality; the range and scope of these properties has not yet been evaluated, however. In tight collaboration with the group of Prof. P. Günter of the Institute of Quantum Electronics at ETH, we employ macromole-

cules as carriers of orientation-dependent electromagnetic functions that withstand conditions at which to date other polymers fail.

Polymers and Inorganic Materials

(Nano)composites with Surface-modified Fillers

Systems of polymers and inorganic materials (composites) are in widespread use in technology and in daily life. The

fillers modify the appearance, the mechanical properties, the thermal and electrical conductivities, the dimensional stability, the permeability, the abrasion resistance, and much more. The long-term stability of such composites is often limited by poor compatibility between polymer and filler at the interface. This insufficiency can be overcome by modification of the fillers' surfaces. We use, e.g. muscovite mica that consists of platelets with an average thickness of typically 1 μm and that we can cleave to average thicknesses below 10 nm. Muscovite contains alkali metal ions at the surface that can be exchanged with organic ions. We have studied these processes and prepared mica covered with an ultrathin layer (0.5–2 nm thickness) of various low- and high-molecular-weight substances. These layers can drastically change the wetting properties and chemical reactivity of the mica surfaces and, therefore, improve the compatibility of mica with a number of polymers or even bind polymers to mica that would otherwise not adhere, e.g. polystyrene or polydimethylsiloxane (see Fig. 6). Some of the modified micas have been used for composite fabrication, and we study the influence of the surface modification on nanocomposites' materials properties. Analogously, we are modifying talcum, calcium carbonate, and other minerals.

Adhesives

Practically all adhesives are polymeric materials. They are used ubiquitously in advanced technological applications. We are engaged in research of adhesion and have, for example, elaborated a new and unique adhesion promoter based on the hitherto unknown surface attachment of polysiloxanes by activation of Si-H

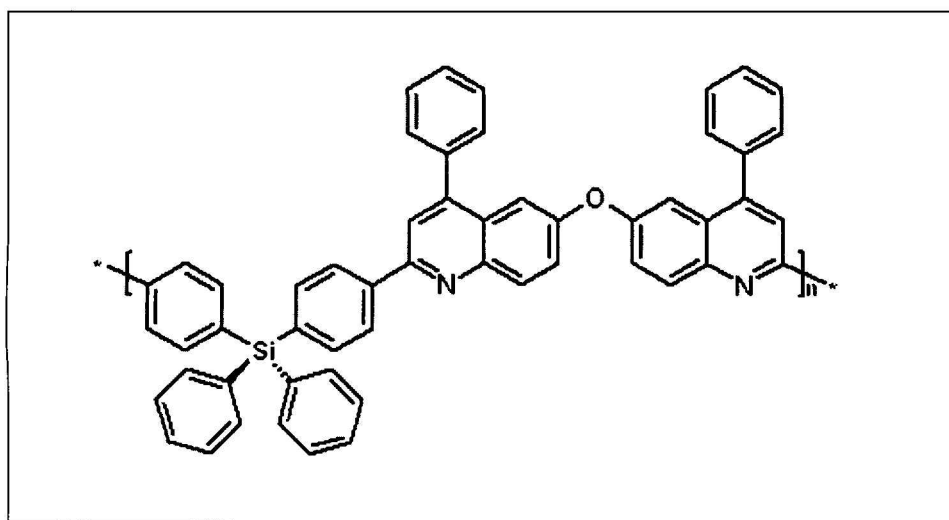


Fig. 5. Fully aromatic polyquinolines, amorphous or crystalline, are high-temperature-resistant functional polymers. The example shown exhibits a glass transition (T_g) at 280 °C (DSC, 2nd heating, 10 °C/min, nitrogen flow) and an onset of decomposition (T_d) at 600 °C (TGA, 20 °C/min, air flow).

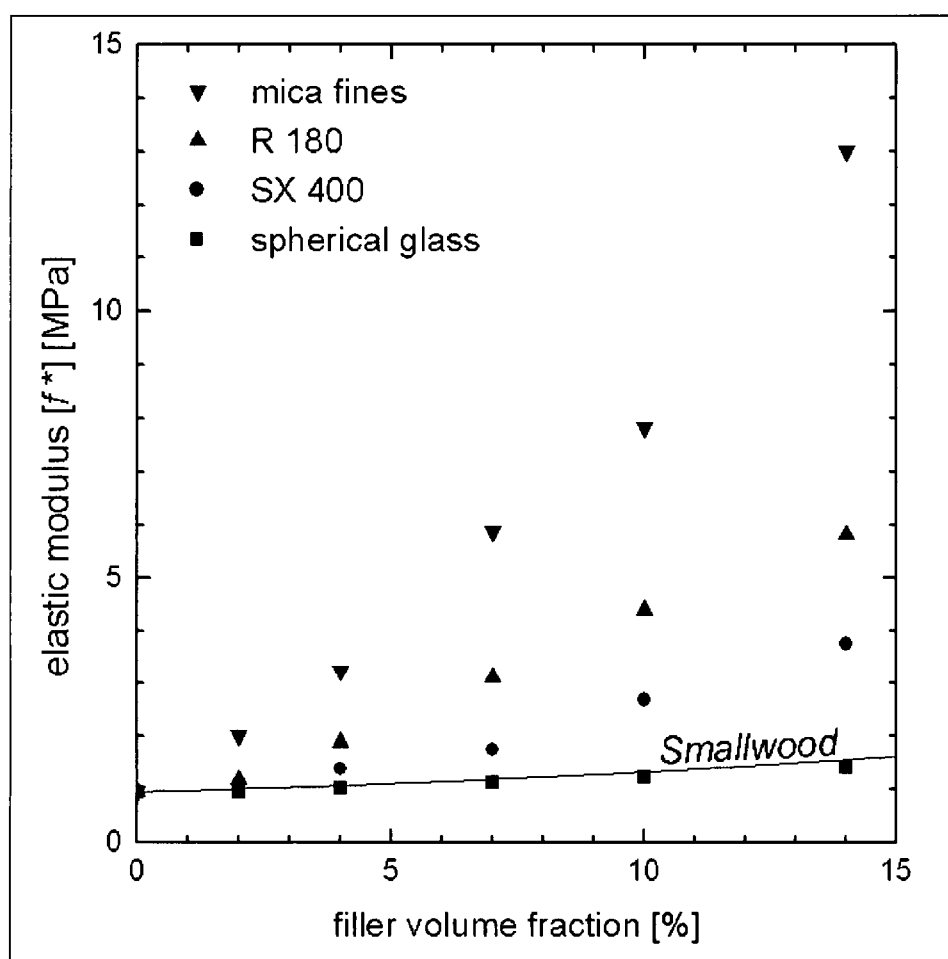


Fig. 6. The elastic modulus of filled, crosslinked polydimethylsiloxane rubber, in function of the filler volume fraction for the random composites with spherical glass (■, aspect ratio = 1), mica SX 400 (●, aspect ratio = 40), mica R 180 (▲, aspect ratio = 95), and mica fines (▼, aspect ratio = 120). The line serves mainly as guide to the eye, but represents the theory by Smallwood ($E/E_0 = 1 + 2.5\phi + 14.1\phi^2$, for random composites with spheres, H.M. Smallwood, *J. Appl. Phys.* 1944, 15, 758).

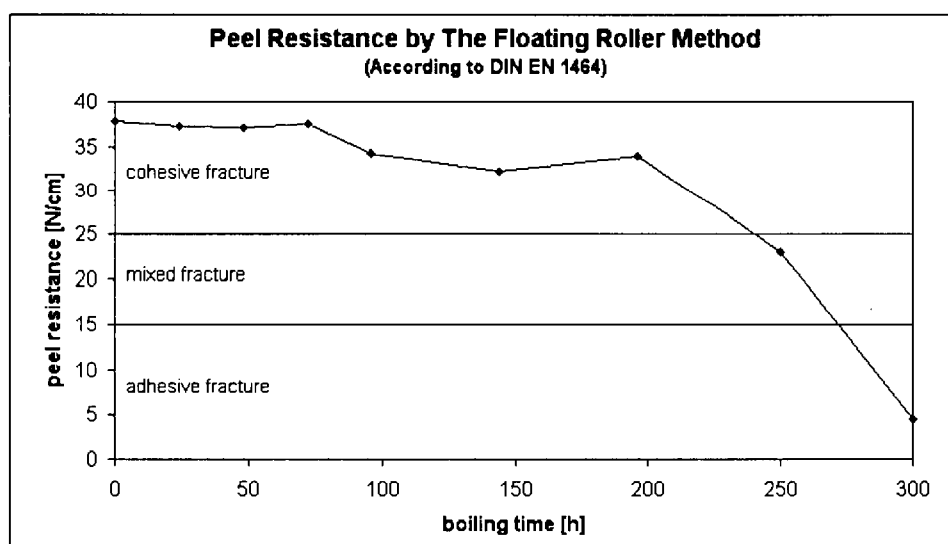


Fig. 7. Peel-resistance tests by the floating roller method according to DIN EN 1464. Plates of aluminum were coated with a monolayer of polyhydromethylsiloxane, activated with a proprietary catalyst. 5 mm of a two-component silicon rubber were injected on top of that monolayer. After curing the silicon rubber, the samples were exposed to boiling water during the indicated time, then the peel-resistance tests were performed. Without coating the plates of aluminum with a monolayer of polyhydromethylsiloxane, no peel resistance is obtained. The system employed here is commercially available (Global Surface AG, <http://www.globalsurface.com/>).

bonds. Depending on the polysiloxane used, the resulting layers (thickness 1–5 nm) contain non-reacted Si-H groups or hydroxyl groups that can further react with other materials systems, on an extraordinarily wide range of materials such as metals, ceramics, glass, wood, stone, concrete, or other polymers. For instance, surfaces modified with Si-H bonds bind two-component silicon rubbers that otherwise do not adhere significantly. The adhesion promoting effect can be retained in boiling water for at least 200 h (see Fig. 7). A number of commercial applications of this system are under development.

Outreach

Two start-up companies have emerged from the group:

Global Surface AG

(<http://www.globalsurface.com/>,

est. 1997 in Zürich), a company that specializes in surface technology and undertakes research and development with the aim of creating science-based solutions to many surface problems. Their primary expertise is in coating surfaces with thin and ultrathin layers with thicknesses from 1 nm, by a revolutionary method.

MatSim GmbH (<http://www.matsim.com/>,

est. 1998 in Zürich), a company that provides expert tools for Materials Simulations. Their software package Palmyra allows the prediction of mechanical properties of heterogeneous solids, such as the resistance of fiber-reinforced polymers, the failure strain of unidirectional composites, the energy absorption properties of foams, or the elasticity and stiffness of polymers with additives.

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