Research News

NMR Imaging of Materials

In the past ten years NMR imaging has developed into a valuable diagnostic tool for clinical applications, because images of arbitrary cross-sections of living objects are obtained in a non-invasive fashion free of radiation hazards.[1] During the same period various efforts have been undertaken to apply NMR imaging to materials. However, for two reasons the results turned out to be of limited significance for practical applications: 1) The NMR signals of nuclei in solids are several orders of magnitude broader than those in liquids, which limits the achievable spatial resolution. Instead of a few Hertz linewidth encountered in medical applications, the resonances of solid materials are several Kilohertz wide. Because of the slow molecular mobility in solids, the anisotropy of the chemical shift and the dipole-dipole interactions of the nuclear spins are not averaged to their isotropic values as in liquids. 2) There seem to be few arguments against dissecting a dead object for analysis.

To circumvent the linewidth restriction, much attention focussed on the imaging of highly mobile species in solids, such as liquids diffused into solids, or on narrow solid-state resonances. Some representative applications are investigations of the pore size and binder distribution in green-state ceramics,[2] the distribution of liquids in polymers,[3] the oil and water contents of sand and rock,[4] and stress induced crystallization of polyisoprene rubber.[5]

To answer these questions, non-invasiveness is not a prerequisite, but for the investigation of properties dependent on the shape or function of the sample it is. Such properties are for instance nonequilibrium distributions of heat or strain, transport phenomena, and the progress and extent of chemical reactions. A few such questions have been addressed employing basically liquid state imaging techniques, for example the temperature distribution in a KBr sample,[6] the cross-linking of polyesters as a function of the flow rate of the resin, changes in viscosity, differential cross-linking before gelation, and catalyst concentration,[7] and the growth and mineralization of bones.[8]

In materials science, however, liquid-state NMR techniques are inadequate for handling the large linewidths, and special solid-state imaging techniques need to be developed. Recently two new significant approaches to solid-state imaging have been demonstrated, which rely upon line-narrowing techniques known in high resolution solid-state NMR spectroscopy.[9] 1) By homonuclear multi-pulse decoupling dipolar broadened lines can be narrowed up to a factor of 400.[10] An application of the technique is shown in Figure 1, which displays the images of a neoprene rubber annulus around a cylindrical tube of adamantane.[11] In Figure a) both, cylinder and annulus are seen. By exploiting differences of relaxation times of these two materials in the rotating frame, the rubber (b) and the adamantane (c) signals can be discriminated. The spatial resolution is about 0.25 mm. 2) Higher resolution, even in truly rigid samples, can be achieved by spinning the sample at the magic angle of 54.7° relative to the magnetic field with speeds of 3 kHz and more. If the magnetic field gradients needed for spatial resolution are rotated with the sample, basically all known imaging methods can be adapted.[12] The sample size, however, is restricted to cylinders smaller than about 12 mm in length and 6 mm in diameter. With such methods, the ultimate spatial resolution in solids is not so much restricted by the linewidth anymore, but rather by the number of nuclei producing the

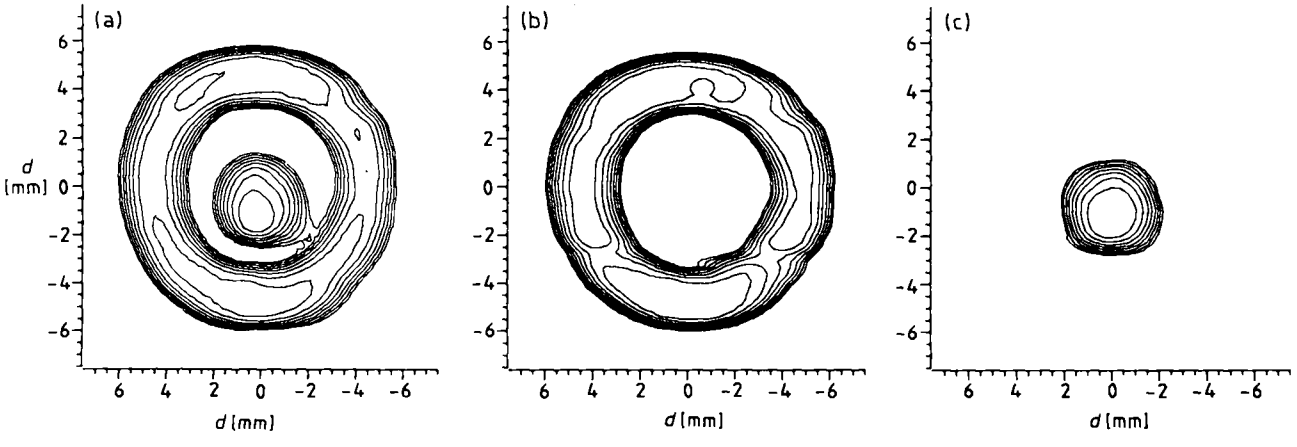

Fig. 1. Solid-state ^{1}H NMR image of an adamantane cylinder in a neoprene rubber annulus (a). The different molecular mobility in the two materials is exploited via the relaxation time in the rotating frame to discriminate the rubber signal (b) from the adamantane signal (c). (Adapted from ref. 11.)

signal. A practicable value is 100 μm. Thus microscopic resolution is not achievable, but other properties of solid materials varying on a macroscopic scale now seem to become amenable to investigation. Examples are the material's response to nonlinear mechanical wear, crazing, locally controlled polymerization, crystallization, and self-organization of molecular segments as well as strain, heat conductivity, convection and diffusion in composite materials.

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Book Reviews

Corrosion of Materials

DECHEMA Corrosion Handbook: Corrosive Agents and their Interaction with Materials, Volume 1. Edited by *D. Behrens*. VCH, Weinheim 1987, 333 pp., bound, DM 775.00.—ISBN 3-527-26652-6

Materials scientists have developed a huge number of technically important materials based on metals, inorganic and organic compounds and composites, suitable for applications which are sometimes very specific. One criterium for choosing a material for a given technical use is its corrosion behavior. However, the prediction of corrosion properties is a rather difficult task due to the complex nature of corrosion processes, involving in a typical case a metallic substrate, a corrosive medium, the hydrodynamic properties of the medium, and the geometric properties of the construction itself. Therefore, a *Corrosion Handbook* collecting together the vast literature and knowledge in this area is highly welcome.

The DECHEMA Corrosion Handbook—a series of at least twelve volumes is planned—is a completely new English edition of the DECHEMA-Werkstoff-Tabelle. The chapters are arranged according to the aggressive media, but instead of being arranged alphabetically these are treated in an apparently random order. Each chapter, which reviews the data concerning one medium, is divided into metallic materials, non-metallic inorganic materials, organic materials and materials with special properties. In this first volume metallic materials predominate. At the beginning of each chapter all materials are classified in a table according to their corrosion properties in the given medium; following this table a detailed description of their corrosion behavior is given. Owing to the very different technical applications for the different materials in the given medium, the ratings in the table may be misleading, if the detailed description is not taken into account. For example, in the chapter "Chlorine" the material gold is classified from resistant to unsuitable due to the fact that on the one hand the contact resistance of Au contacts is high in chlorine atmospheres, whereas on the other hand Au has only limited resistance to high temperature corrosion. In the same table high alloy cast iron is classified as fairly resistant, yet in the detailed description it is stated that not much literature is available about the corrosion of this material in chlorine atmospheres, and therefore the rating is based only on very specific applications.

It is therefore essential for the user of this handbook to read and understand the detailed description and not to rely on the ratings in the well presented tables by themselves. In order to understand the data presented in the different chapters, the reader needs to have a sound background in corrosion science, as the handbook offers only very limited background information concerning the basic mechanisms of corrosion processes. As some interested users might not have this background in electrochemistry or physical chemistry of solids, the reviewer would have liked the first chapter "General remarks and instructions for use" to contain much more information than the one page can offer to the reader. In this chapter only corrosion rates are classified, by which the different materials are evaluated. There is a lengthy explanation of how to convert