

The Interdisciplinary Workshop
on
STRUCTURE AND PROPERTIES OF AMORPHOUS SOLIDS

June 3-6, 1984

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ABSTRACTS

INVITED SPEAKERS

LOCAL STRUCTURE OF METALLIC GLASSES: COMPUTER MODELS

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Starting with the random close packed hard sphere models we demonstrate their inadequacy when considering the relationship between the atomic structure and properties of glasses and show that consideration of atomic interactions which include both the repulsive and attractive part is essential. The analysis of the local atomic structure in terms of atomic level hydrostatic and shear stresses is then introduced and the relationship of these quantities to the local topology discussed. Analogy with crystal defects is then emphasized and it is argued that two distinct "defects" characterized by hydrostatic tension or compression and shear stresses, respectively, must be considered. Using these concepts the structural relaxation, plastic deformation and glass formation are discussed.

"Order, Frustration and Defects in Glasses"

D.R. Nelson

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NO ABSTRACT AVAILABLE

Structural Models of Amorphous Polymers

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Abstract

Macroscopical properties of amorphous polymers are known to depend strongly on the spatial as well as orientational distribution of the building units of the chain molecules. The structure can to a good approximation be represented in terms of singlet and pair distribution functions.

Experimental methods are described which were used to determine these functions for amorphous polymers and results are reported for amorphous materials composed of flexible chains, semi-flexible chains as well as of chains containing rigid units. The spatial order is usually short-ranged and predominantly determined by local chain conformations. The orientational order is also short-ranged for flexible chains as well as for semi-flexible chains and becomes long-ranged in the case of chains containing rigid units. The local orientational order depends again strongly on the local chain conformation.

Thermal fluctuations of the density, the orientation and the concentration (in polymer blends) are discussed with respect to this structural aspects.

STRUCTURE OF GLASSY POLYMER BY NEUTRON SCATTERING

CHARLES C. HAN

NATIONAL BUREAU OF STANDARDS

Small angle neutron scattering provide a unique opportunity for studying molecular conformation of polymers under various conditions. Scattering principle and instrumentation at NBS will be reviewed. Single chain conformation studies will be discussed. The block chain conformation in microphase separated system will be presented. The anisotropic conformation of a block chain as well as the bulk structure information can be extracted simultaneously in this case. Finally, the critical fluctuation of a binary polymer blends may be described.

Abstract for Workshop of Division of Polymer Chemistry

P. Haasen (University of Goettingen, on leave at Stanford University)

"Microstructure of Metglasses as seen by FIM-Atom Probe"

The motivation for our work in Goettingen is the embrittlement observed when metallic glasses are annealed below the crystallization temperature. As neutron irradiation studies by R. Wagner et al show there are two likely reasons for that: loss of free volume and decomposition in the amorphous state. The latter is studied by the field ion microscope combined with a time of flight mass spectrometer called atom probe. The instrument built in Goettingen by R. Wagner and J. Piller is described. It has been applied to the study of 3 glasses so far:

1. $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ (J. Piller)
2. $\text{Ni}_{60}\text{Nb}_{40}$ (R. Gruene)
3. $\text{Ti}_{50}\text{Zr}_{10}\text{Be}_{40}$ (M. Oehring)

The results will be discussed in connection with the embrittlement of the three glasses. Conclusions are drawn with respect to the decomposition and formation of glassy alloys quenched into deep eutectics.

"Structure of Glasses by Anomalous and Energy Dispersive
X-ray Scattering Techniques"

T. Egami

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NO ABSTRACT AVAILABLE

CREEP OF METALLIC GLASSES

F. Spaepen

All glasses, metallic as well as oxide or polymeric ones, exhibit structural relaxation. As a result, all physical properties change continuously with time. Most strongly affected are the atomic transport rates, such as the diffusivity and the viscosity.

Viscosity measurements near or below T_g are made in creep experiments. Bimolecular relaxation kinetics, well known in oxide glasses, have also been observed in metallic glasses. The equilibrium viscosity near T_g can only be measured accurately if the effects of structural relaxation are taken into account.

Diffusivity measurements on metallic glasses are difficult, since above 10^{-16} cm²/sec, the glasses crystallize rapidly. The study of compositionally modulated films, which allows measurements down to 10^{-23} cm²/sec will be presented in detail. The relation between diffusivity and viscosity (magnitudes, temperature dependence, relaxation behavior) will be discussed.

Chain Entanglement, Deformation and Fracture of Polymer Glasses

A.M. Donald, Cavendish Laboratory, Cambridge, England.

The deformation behaviour of polymeric glasses is profoundly affected by the macromolecular nature of the polymer chains. As well as shear processes, which involve only local segmental motions, crazes form before fracture. These crazes possess a void-fibril structure, the fibrils (which possess molecular orientation) spanning the two craze surfaces and rendering the craze load-bearing. Such structures are stable because the polymer chains are highly entangled.

In this talk, attention will be focussed on the parameters of the entanglement network which control the craze structure. Factors affecting the competition between shear and crazing will also be examined. From consideration of these two subjects, it becomes possible to assess whether a given polymer (with known molecular properties) will exhibit brittle or ductile behaviour under particular experimental conditions.

"Mechanisms of Ion Diffusion in Glasses"

N.L. Peterson

Materials Science Division
Argonne National Lab

NO ABSTRACT AVAILABLE

"Chemistry of Slow Crack Propagation in Glasses"

S. Wiederhorn

Ceramic and Inorganic Materials Division
National Bureau of Standards

NO ABSTRACT AVAILABLE

Mechanisms of Non-Fickian Diffusion

in Polymer Glass

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Many apparently non-Fickian examples of diffusion and solvent penetration can be adequately described using Ficks equations when they are solved with diffusion coefficient as a known function of concentration. There is however a range of sorption processes in polymer glasses for which even a sophisticated Fickian approach is inadequate. Such behaviour is often referred to as CASE II and is characterised by linear kinetics and the penetration of sorbent behind a sharply defined front.

A detailed study of the CASE II process has been made for the system PMMA-methanol, and a model developed in which the mechanical response of the polymer to the thermodynamic (osmotic) pressure exerted by the penetrant is rate determining. The model not only describes the phenomenon but also suggests different experiments which probe the physical properties of the glassy state.

HYDROGEN DIFFUSION IN METALLIC GLASSES

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The thermally-activated motion of hydrogen atoms in metallic glasses can be studied by two different mechanical relaxation phenomena. A short-range reorientation relaxation, involving motion between orientationally-distinguishable adjacent sites, is manifest as an internal friction peak in dynamical measurements at audio frequencies. Due to its short-range nature, the relaxation serves as a probe of the atomic-scale disorder present in the glassy host. By contrast, the second relaxation process is a striking and rare example of a process with a single relaxation time in a disordered material. This second phenomenon, known as the Gorsky relaxation, can be observed by static bending experiments which effectively squeeze hydrogen from one side of the sample to the other and thereby provide the long-range diffusion coefficient. In contrast to the highly non-classical behavior of hydrogen in the crystalline body-centered cubic metals, it will be shown that hydrogen appears to be a quasi-classical defect in metallic glasses, both with respect to its diffusion behavior and its elastic dipole strength. In principle, use of the Gorsky relaxation for diffusion measurements is not restricted to the case of hydrogen, and the prospects for its wider use will be discussed. It will also be shown that sorption-induced bending of a bilayer strip may be a more practical alternative to the Gorsky relaxation in certain applications, such as the measurement of moisture diffusion in polymeric materials.

"Amorphous Alloys by Ion Beam Mixing: Structure and Chemistry"

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Ion beam modification of the outer layers of solids can be achieved by depositing a metal-film on the substrate and bombarding with energetic ions which intermix - ion beam mixing - the film and the substrate. Experimental investigations on ion-induced reactions have shown that ion mixing is well suited for metastable phase formation in metal-metal systems, in that both amorphous and crystalline phases can be formed. With ion irradiation, crystalline phases of simple structures, such as solid solutions or simple cubics, can be formed while amorphous layers are formed with more complex structures. These phase transformations are illustrated by studies of ion-mixing of Al/metal layers using electron diffraction and Rutherford backscattering (RBS). From these and other studies one can make predictions of the composition and structure of intermixed layers.

"Recrystallization Properties of Ion-Beam-Amorphized Si and Silicides"

S.S. Lau

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NO ABSTRACT AVAILABLE

POSTER SESSION

MODIFICATION AND STUDY OF ORGANIC FILMS USING HIGH ENERGY ION BEAMS

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ABSTRACT

Recent results on the effect of high energy ion beam irradiation in polymeric and non-polymeric organic films are reviewed in this paper. High energy ions (< 10 keV/amu) deposit a large amount of energy (\sim several eV/atom) in ionizing the electrons of the target atoms. This results in significant destruction of bonds in the films as a result of which polymers undergo rapid dissociation. The study of transient emission of molecular species produced by an ion pulse has been shown to yield information about the diffusion and reaction kinetics of various molecules in the polymer. The fact that polymers undergo dissociation and those atoms which form volatile species are selectively depleted from the film could be utilized in producing useful inorganic composites by ion bombardment of polymers; hard SiC composite films, for example.

The structural and chemical properties of the organic films were investigated by UV-visible, infrared (IR), electron spin resonance (ESR) and Raman spectroscopy, ESCA and Rutherford back-scattering (RBS) measurements. In most cases, the UV-visible, IR and Raman spectra show the loss of the initial molecular structure at low irradiation doses (10^{13} - 10^{14} cm $^{-2}$) followed by the appearance, at high doses, of a spectrum almost similar to that observed for amorphous carbon. Thus, eventually the organic films dissociate to form a predominantly carbon containing film which exhibits interesting electronic transport properties. Experiments on ion irradiated, pure carbon films indicate that a metallic form of carbon is produced from the organic films at high irradiation doses. Electron energy loss and transmission electron microscopic studies reveal the formation of micro-graphitic regions in these films with the graphite planes oriented parallel to the film with correlation lengths of ~ 10 - 20 Å. Crystalline graphite has a small overlap of the conduction and valence bands (~ 30 meV), and consequently a low carrier density ($\sim 10^{18}$ cm $^{-3}$). We believe the modified carbon films to have larger overlap of the bands (~ 1 eV) at the Fermi level, due to significant smearing of the carrier energy associated with the short scattering (correlation) lengths. While pyrolysis and ion irradiation produce similar end results, ion irradiation can yield ultimately higher carrier densities in these films as the ion-annealing process is self-limiting in terms of the extent of crystalline order produced in the film.

Diffusion of Water Amorphous Epoxy Resins and
Their Carbon Composites*

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Abstract

The diffusion of water in a neat epoxy resin and carbon-epoxy composites was investigated as functions of humidity and temperature. Test coupons were prepared from the resin (Ciba-Geigy MY720/Eporal), a cross-ply graphite fiber composite, and a uniaxial graphite cloth composite. The coupons were exposed at 35°, 50°, 65°, and 80°C while at 100% RH or immersed in water.

The diffusion coefficients were determined by: 1) a new and unique method, precision abrasion mass spectrometry (PAMS) and 2) gravimetric analysis. PAMS is a technique to measure qualitatively and quantitatively the distribution of volatile compounds in an intractable matrix. Solid samples are precisely abraded inside the ion-source housing of a time-of-flight mass spectrometer where the volatile compounds released are ionized, mass analyzed, detected, and recorded. The intensity of selected ions is measured as a function of time during constant abrading, thus generating a spatial distribution profile. A least-squares analysis is used to fit the experimental data to a series solution of Fick's second law. The diffusion coefficient and surface concentration (solubility) data on the Fickian and non-Fickian diffusion process will be presented.

*This research was conducted under the McDonnell Douglas Independent Research and Development program.

RUTHERFORD BACKSCATTERING SPECTROMETRY (RBS)
STUDIES OF CASE II DIFFUSION IN POLYSTYRENE

BY

R.C. LASKY, E.J. KRAMER, P.J. MILLS

J.W. MAYER, C.J. PALMSTROM

RBS is used to measure concentration profiles of iodated hexane into glassy polystyrene. The excellent depth resolution (<30nm) of RBS allows one to investigate, for the first time, the detailed nature of the Case II diffusion front. The concentration of the penetrant drops off abruptly, in 100nm, at the front; but then decays exponentially with distance in the glass ahead of it. The diffusing front has been modelled as a moving source with a Fickian precursor. Front velocities, precursor diffusion coefficients and weight gain are obtained, from the RBS data, as a function of temperature.

FORWARD RECOIL SPECTROMETRY (FRS) STUDIES
OF POLYMER-POLYMER INTERDIFFUSION

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Edward J. Kramer

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These experiments involve measuring the concentration profile of a thin layer (<30nm) of deuterated polymer diffusing into a much thicker film of hydrogenated polymer. High energy $^2\text{He}^{++}$ ($E_0=3\text{MeV}$) ions are directed at the film at glancing incidence. ^1H and ^2H nuclei in the film recoil from the surface and near surface regions as a result of elastic collisions with the incoming $^2\text{He}^{++}$ ions. After passing through a foil, which stops the forward scattered $^2\text{He}^{++}$ ions, the energies of the hydrogen and deuterium nuclei are measured with an energy sensitive detector. Since ^2H recoiling from the surface receive a much larger fraction ($\sim 2/3$ rd) of the incident energy E_0 than do ^1H ($\sim 1/2$), the surface peak due to ^2H is well separated from that due to ^1H . Deuterium and hydrogen nuclei below the surface recoil with a lower energy due to the energy losses (electronic) suffered by the $^2\text{He}^{++}$, $^1\text{H}^+$ and $^2\text{H}^+$ ions as they traverse the overlying polymer. The forward recoil spectrum thus obtained may be analysed to find the d-polymer concentration as a function of depth. While the FRS technique was first described a few years ago for profiling implanted hydrogen and deuterium in metals, the application to polymer diffusion has great advantages. Entire diffusion profiles can be measured in a few minutes, with high sensitivity (0.1vol% d-polymer). With the depth resolution achieved (80nm), diffusion coefficients D between 10^{-11} cm^2/sec and 10^{-15} cm^2/sec may be measured with diffusion times less than one day. Perhaps best of all, only a few milligrams of deuterated polymer are sufficient to allow one to determine D for many samples. We have applied FRS to measuring the diffusion of monodisperse deuterated polystyrene (PS) of molecular weight M into monodisperse hydrogenated PS of molecular weight P at a temperature of 170°C . While for large P , measured D values are consistent with a reptation mechanism for the diffusion of M -chains ($D \propto M^{-2}$, independent of P), D increases rapidly as P is decreased below P^* . The value of P^* is well above M_c , the critical molecular weight for the onset of entanglement effects in viscous flow, and increases with increasing M . The results are in quantitative agreement with $D = D_R + D_{CR}$, where D_{CR} is the diffusion coefficient of the M -chain by constraint release of the "tube" formed by the surrounding P -chains.

FRACTURE IN EPOXY RESINS

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ABSTRACT

The fracture surfaces of at least certain rigid epoxy resins have been found by scanning electron microscopy (SEM) to have a greatly confused structure. Such a structure is usually desired because it implies an enhanced fracture energy, which contributes to a larger tensile strength and toughness. Key to the fracture surface structure seems to be the propagation of cracks having an array of fingers jutting out ahead of the crack. Because the fingers are subject to local stresses and material inhomogeneities, they tend to lose coherence and to move upward or downward individually to various planes above and below the main fracture plane. The occurrence of fingers ahead of the main failure have been nicely documented by Kramer and coworkers for crazes in thermoplastics. In this instance, the fingers are suggested to arise from a Taylor meniscus instability at the craze front. A similar mechanism is suggested for the fingers preceding the cracks in the epoxy resins studied by us, although the periodicity of the fingers of 0.5 μm in the epoxy resins, as indicated by the resulting fracture surface texture, is significantly larger than the periodicity of 20-30 nm seen for the crazes.

"Pulsed Laser Spectroscopic Study of the Photoisomerization of
Azo Labels at Three Different Locations on a Polystyrene Chain"

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Abstract

Azobenzene chromophores have been incorporated as molecular labels at three specific sites on a polystyrene chain; the chain end, the chain center or as the side group. Trans \rightleftharpoons cis photoisomerization kinetic behavior of azo labels has been studied both in dilute solution and in the glassy state at 20°C, using nanosecond pulsed laser spectroscopy which reduced the measurement time to only two seconds. In dilute solution, a small difference in the label's photoisomerization behavior has been observed at different sites of the chain; the end label can photoisomerize a little faster than the center label or the side label. A much greater difference is observed in the glassy state, especially between the end label and the center label. Assuming that in the glassy state, only a certain fraction of the label can isomerize with the same rate as in dilute solution, only 8% of the center label is found to photoisomerize while about 45% of the chain end or the side group photoisomerizes at 20°C. The experimental results are discussed in view of the theoretical predictions based on the free volume size distribution theory of Robertson, which was applied to meet the photoisomerization requirement of the azobenzene label. This theory predicts that 23% of the azo label can isomerize at 20°C. In view of the packing differences and the resulting free volume differences in the chain end versus the chain center, the trends between the theoretical value and the experimental values seem reasonable. Kinetics of physical aging at 10°C below T_g as monitored by our labels are found to be also a function of the sites in polystyrene. Comparisons made between our data and the volume relaxation data of Kovacs shed interesting insights as to the aging process.

Molecular Modeling of a Vinyl Polymer Glass

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We have developed a method for simulating the structure of well-relaxed amorphous vinyl polymer glasses on the atomistic level. Our system consists of a cube of atactic polypropylene with periodic boundaries, packed with chain segments of a realistic glass-density. Individual hydrogen and carbon atoms and methyl groups are treated explicitly.

An initial guess structure is randomly generated, using a Rotational Isomeric State "equivalent Markov process," modified to incorporate long-range interactions. This structure is subsequently relaxed by straightforward potential energy minimization, based on analytical derivations of the system energy with respect to the microscopic degrees of freedom (Eulerian and bond rotation angles). Optimization is stagewise, employing a technique of "blowing up" atomic radii (which saves computer time) and an efficient quasi-Newton algorithm.

Pair distribution functions and bond direction correlation functions computed from the structure thus obtained show no evidence of correlation effects beyond 5 Å. A theoretical estimate of the cohesive energy density agrees very well with experiment. Current work focuses on the prediction of mechanical properties by simulating deformation of our model structures.

Nonlinear Viscoelastic Behavior of Glassy Polymers:
Experimental Results and Theoretical Model

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The time-dependent behavior of polymers can be significantly modified by the application of stress, giving rise to nonlinear effects. The ability to describe this stress or structure dependent relaxation spectrum is the key to formulating a model for predicting the nonlinear mechanical properties of polymers. In this paper we describe a novel stress relaxation technique that probes the relaxation spectra of glassy polycarbonate at various strain levels including nonlinear strains. In the experiment, an initial strain is applied. After some time has elapsed, the relaxation behavior of the structure is probed with a small second strain step. Results of these second strain steps reveal that they can be fitted to the Williams-Watts function with a strain dependent β . The spectrum narrows and the effective relaxation time τ_p becomes shorter on increasing strain. The strain dependences of τ_p and β are strongly correlated. This important aspect has led us to construct a model of relaxation under nonlinear deformations. These results are used to predict the stress-strain curves of PC at various temperatures and strain rates. The predictions agree well with experimental results. The same model has been shown to be applicable to polymer melt rheology, the isotope mass effect in glasses, and other topics discussed at this conference.

