

# SYMPOSIUM AA

## Materials Science of Food–Processing-Structure-Property Relationships

December 1 – 2, 1999

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SESSION AA1:

Chair: Athene M. Donald  
Wednesday Morning, December 1, 1999  
Provincetown/Orleans (M)

**8:30 AM \*AA1.1**

**THE MATERIALS SCIENCE OF CHOCOLATE: CASTING AND SOLIDIFICATION.** Peter J. Fryer, Heather Tewkesbury<sup>1</sup>, Kerstin Pinschower and Andrew GF Stapley, School of Chemical Engineering, University of Birmingham, UNITED KINGDOM; <sup>1</sup>Cadbury Ltd, Bournville, Birmingham, UNITED KINGDOM.

Chocolate is a complex polymorphic material whose consumer acceptability depends critically on it having the correct crystal form. There are at least five polymorphs that have been identified; crystallisation is very dependent on the composition of the material. Chocolate is given a tempering pre-treatment prior to casting; if this is incorrectly carried out, as well as being unacceptable to the customer, the material may not demould. Understanding the effect of tempering on the final product quality is thus vital. The rate and extent of crystallisation, as well as the crystal form, is a strong function of the temperature, time and shear profile which the material has received. The crystallisation of chocolate has been followed using differential scanning calorimetry to study the thermal events in cooling for samples given defined process histories. Critical combinations of temperature and shear have been identified to ensure that the material adopts the correct form on solidification. The effective specific heat of chocolate varies greatly as a function of temperature and cooling rate, because of the amount of latent heat released. The temperature changes in casting of chocolate have been modelled using a commercial CFD program. Over a range of cooling rates of practical interest, it is possible to model the cooling using data for effective specific heat capacity, i.e. to approximate the kinetics of the crystallisation process. The shape change on cooling has been studied using non-invasive surface profiling to follow mould shrinkage: differences in shape due to different temper conditions can be clearly identified.

**9:00 AM \*AA1.2**

**PHASE TRANSITIONS AND POLYMORPHISM IN LIPID FOODS: TEXTURE AND STABILITY.** Richard Hartel, University of Wisconsin, Department of Food Science, Madison, WI.

Controlling crystallization and polymorphism of lipids is important to the texture, stability and overall quality of many foods. However, due to the complexity of natural fats, our understanding of the principles of crystallization in food products is generally quite limited. Compounding these difficulties is the lack of techniques for observation of lipid crystalline structure available to us. Recent efforts using confocal microscopy have allowed us to visualize the effects of processing conditions on crystalline structure of different model fat systems. Differences in crystalline structure (number, size, distribution, shape, polymorph, etc.) lead to different mechanical properties and, in some cases, to stability of the food product during storage. In two model systems (milk fat fractions and canola oil), processing parameters such as cooling rate, agitation rate, and crystallization temperature had significant effect on crystalline structure and mechanical properties of the semi-solid material. However, subsequent changes in mechanical properties during storage were different for the two model systems. The model system made up of two milk fat fractions exhibited an increased hardness with storage time, whereas the model system made up of a hard milk fat fraction mixed with canola oil did not show this change. This difference was related to the structural changes (sintering, etc.) in the crystalline material over time.

**10:00 AM \*AA1.3**

**MIXED BIOPOLYMER COMPOSITES.** Ian Norton, Unilever Research, Colworth House, Sharnbrook, Bedfordshire, UNITED KINGDOM.

Biopolymers (Polysaccharides and Proteins) are used in the Food Industry to impart texture and appearance properties to fabricated foods. It is quite often the case that a single biopolymer is incapable of delivering all the desired properties. Although in the chemical industries this problem can be overcome by chemical and biochemical modification of the polymeric species, this is not an option open to the Food industry due to constraints on Food additives. It is with this background that we have studied mixed biopolymer systems and in particular biopolymer composites. Within this talk I will cover the mechanism of formation, kinetic trapping and flow modification of composite structures and then cover some of the mechanical consequences of the microstructures formed.

**10:30 AM AA1.4**

**STUDIES OF PHASE SEPARATION UNDER DYNAMIC CONDITIONS.** Niklas Loren, Anne-Marie Hermansson, SIK, The Swedish Institute for Food and Biotechnology, Gothenburg, SWEDEN.

There is an increasing interest to control phase-separation of biopolymer mixtures in order to impart the desired textural properties and stability to food products such as spreads, dressings, yoghurts and low-fat products. When phase separation occurs together with gel formation, the structure can be trapped by the formation of a three-dimensional biopolymer network. In this work mixed biopolymer systems have been studied by confocal laser scanning microscopy (CLSM) equipped with a Linkam table, transmission electron microscopy (TEM) and image analysis. The approach used is mainly stereological image analysis. By CLSM it is possible to follow the development of the microstructure with time and to obtain three-dimensional microstructures by combining confocal planes at different depths. Results have shown that the resulting microstructure depends considerably on the cooling rate, the composition and the temperature of phase separation. They also stress the importance of pH and the differences between different types of the same material. Three different zones of phase separation kinetics have been established due to the relative rates of phase separation and gel formation. On going research deals with the kinetics of phase separation and tries to establish further knowledge about the structural development with time for various morphologies such as droplets, bicontinuous and double phase separation morphologies. Mechanisms considered of importance for the kinetics of phase separation and gel formation are spinodal decomposition, nucleation and growth, diffusion and hydrodynamic coarsening. The main objectives with our research are to implement new image analysis methods to the field of mixed biopolymers and to understand more about the mechanisms of phase separation in connection to gel formation. The project is a part of an ongoing EU-project Mixed biopolymer- Mechanism and application of phase separation (FAIR-CT96-1015).

**10:45 AM AA1.5**

**QUANTITATIVE ASSESSMENT OF PHASE COMPOSITION IN AND MORPHOLOGY OF TWO-PHASE GELATIN PECTIN GELS USING FLUORESCENCE-BASED ANALYSIS,** Tor S. Nordmark and Gregory R. Ziegler, The Pennsylvania State University, Department of Food Science, University Park, PA.

The interest in gums among manufacturers of prepared foods and confectioneries has markedly increased in recent years, since gums are valuable as texture and flavor modifiers, stabilizers, and fibers. The employment of binary gels appears to offer increased opportunities to improved performance. A technique for quantitative determination of the concentrations of polysaccharide and protein in the phases by fluorometry has been developed and compared with chemical analysis. In the first case, a general method for fluorescent labeling of carbohydrate polymers was developed. For the latter purpose, two micro-assays were developed on the basis of recent polymer macro-assays. A blend of low-methoxyl pectin and gelatin B was used as model system. The commercial components were both subjected to multi-step purification procedures before they were employed in the experiments. Phase separation was initiated by the addition of salt to aqueous solutions of the two polymers. Samples were withdrawn for microscopy after different holding times at 60°C. Tie-lines were determined while using both the fluorescent and chemical methods. The results from these methods were in fair agreement with each other and with literature data. A three-phase region was discovered in the pseudo-ternary phase diagram. The morphology of double-labeled gels was also studied in two and three dimensions in a confocal scanning laser microscope. The results show promise for the quantitative assessment of phases that contain carbohydrate polymers and in the study of morphological changes that occur during thermo-mechanical processing. Keywords: Gum, low-methoxyl pectin, gelatin, fluorescence, morphology, phase diagram.

**11:00 AM AA1.6**

**THE STATE DIAGRAM OF PHASE SEPARATED BIOPOLYMER BLENDS.** Imad A. Farhat; John R. Mitchell; Z. Mousia; Division of Food Sciences, University of Nottingham, UNITED KINGDOM.

The role of unequal distribution of water on the glass-rubber transitions of phase separated, low water content (less than 30 percent wet weight basis) gelatin-amylopectin extrudates was studied for different blend compositions. FTIR microspectroscopy indicated a high degree of phase separation where amylopectin-rich domains (50-80 microns diameter) could be clearly identified in the continuous gelatin matrix. The thermograms of these blends exhibited 2 transitions confirming the existence of the 2 phases. The glass-transition temperatures for each of the 2 phases were successfully predicted based on the existing values for the binary systems if the

unequal partitioning of the plasticizer between the polysaccharide and the protein was accounted for. The selective hydration values were estimated using the water vapour sorption/desorption isotherms of the individual biopolymer components of the blend. Finally, a fraction of these blends were stored in water content and temperature conditions where the retrogradation of amylopectin could proceed within the timescale of the experiment. This enabled the investigation of the role of recrystallization of a component of the blend on the water distribution and subsequently the glass transition temperatures of the amorphous components of blend.

#### 11:15 AM AA1.7

**PARTITION OF PROTEINS IN THE AQUEOUS GUAR/DEXTRAN TWO-PHASE SYSTEM AND CONSEQUENCES ON THE PHASE DIAGRAM.** Frédéric Simonet, Catherine Garnier, Jean-Louis Doublier, INRA-UPCM, Nantes, FRANCE.

Texture and stability of food systems are usually governed by the interactions between macromolecular species in the aqueous medium. Many polysaccharide/polysaccharide and polysaccharide/protein aqueous systems have already been studied and in many cases phase separation due to thermodynamic incompatibility has been evidenced. Still, these mixtures remain far from real food products that usually contain more than two macromolecular species. The present work aims at studying aqueous systems containing two polysaccharides and one protein, a phase separation occurring between the two polymers. In such systems, a partition of the protein between both phases is generally observed. The guar/dextran two-phase system was chosen as a model of segregative system and the added protein was either a globular protein (bovine serum albumin or  $\beta$ -lactoglobulin) or micellar casein. The influence of ionic strength (NaCl), protein concentration and polymer concentration on the partition coefficient was investigated. In all cases, the protein was more concentrated in the dextran-enriched phase than in the guar-rich one. For globular proteins, the general trends established in the literature dealing with other aqueous two-phase systems like polyethyleneoxide/dextran were nearly verified. Micellar casein however displayed a different behavior, giving a more uneven partition and phase separation at concentrations up to 0.5%. This difference has been attributed to the larger size of the particle. Simultaneously, the modifications of the guar/dextran phase diagram in the presence of proteins were investigated. It was shown that the addition of protein up to 2% did not affect the thermodynamic features of this system.

#### 11:30 AM AA1.8

**THE PROPERTIES OF BLENDS OF VARIOUS PROTEINS WITH POLY (HYDROXY ESTER ETHER).** Chaohua Wang, Jerold Bietz, J.L. Willet, and Craig Carriere, National Center for Agriculture Utilization Research, US Department of Agriculture, Peoria, IL.

Poly(hydroxy ester ether) (PHEE) is a recently developed bisphenol A ether-based synthetic biodegradable thermoplastic polymer. It was found that the compatibility and mechanical properties of the blends of PHEE with many renewable protein-containing materials strongly depend on their solubility and hydrophobicity. Morphological analyses by scanning electron microscopy showed that many renewable materials could be used as fillers. Mechanical (tensile testing) properties including Young's modulus, percent elongation, and tensile yield strength, indicating optimal end-uses of products formulated from these materials, were determined. It was found that these renewable materials could be used to adjust mechanical properties of ultimate products. Thermal analyses by differential scanning calorimetry were carried out to reveal their inherent properties and compatibility of various blends at different temperatures, providing information valuable for the molding applications. It was concluded that PHEE filled with inexpensive and renewable biodegradable polymers could be an attractive system for biodegradable, molded applications. This research was conducted under CRADA 58-3K95-9-717 between Agricultural Research Service and Biotechnology Research and Development Corporation.

#### 11:45 AM AA1.9

**TENSION TESTS ON MIXED GELATIN:MALTODEXTRIN COMPOSITE GELS.** Valery Normand, Kevin Plucknett and Dudley Ferdinando, Unilever Research, Colworth Laboratory, Sharnbrook, Bedfordshire, UNITED KINGDOM.

The work presented here deals with composite biopolymer gel system behaviour when submitted to large deformation. As an example, the system gelatin (Lime hide) : Maltodextrin (SA2) is investigated under conventional tension tests. The binodal and the tie line directions of the phase diagram have been defined using classical techniques. Mixtures of these two biopolymers behave as water in water emulsion system at 60°C and under high concentration conditions, forming spherical particles of one biopolymer dominant phase imbedded in a continuous phase dominated by the presence of the other biopolymer. Composite gels were produced from cooling rapidly incompatible

mixtures belonging to the same tie line, which kinetically trapped the structure formed at high temperature. The composite gel samples were tested using both mechanical and Confocal Scanning Laser Microscopy (CSLM) techniques. This study highlights the effect of the phase volume of the included phase on the fracture properties of the composite. The experimental results have been explained according to the properties of individual phases in term of true strain and true stress. CSLM pictures of the fracture edges are presented showing the microstructure damages caused by the test at and away from the fracture surface. On the one hand, evidences of debonding of SA2 rich particles close to the edge of the fracture are shown when the gelatin rich phase is the continuous phase, which suggests weak interface properties. On the other hand, gelatin rich particles present apparent plastic deformation without recovery at the fracture surface of SA2 rich continuous phase, which suggests stretching of the particles in a normal direction to the fracture line.

#### SESSION AA2:

Chair: Peter J. Fryer

Wednesday Afternoon, December 1, 1999  
Provincetown/Orleans (M)

#### 1:30 PM \*AA2.1

**SIMULATION TOOLS FOR STRUCTURES OF FOODS.**

John Melrose, Polymers & Colloids Group, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

The talk will review progress in developing simulation tools for modelling foods at the level of mesoscale structure with the aim to study flow and mechanical properties. Results from models of colloid particle gels and networks both in the bulk and in layers will be reported. These will include the stress strain and rupture response and the aging of such structures. The modelling of cellular structures from dry foams, fluid filled foams, wet foams through too concentrated emulsions are a particular challenge. The talk will assess the technical issues and current status of this area.

#### 2:00 PM AA2.2

**COMPUTER SIMULATION OF AGGLOMERATE-GROWTH AND BREAK-UP IN WET GRANULATION OF FINE POWDERS.**

Gabriel I. Tardos, The City College of The City University of New York, Department of Chemical Engineering, New York, NY.

Granulation is a particle enlargement process in which fine powdery particles are agglomerated into larger granules. Agglomeration in wet granulation is achieved by spraying onto a shearing powder mass a "binder" fluid that binds the particles together. The granulation model presented here is essentially a computer simulation of a shear flow of solid particles, some of which are wet (covered by binder and therefore "sticky") while the rest are dry.

The numerical simulations study two distinct regimes of agglomeration found in a typical granulator: that of granule growth and subsequent breakup. During granule growth-simulations final granule size (and shape) distributions can be obtained by analyzing the size and shape of formed granules using a pattern-recognition routine. A second kind of simulation, also using rapid granular flow modeling, follows the rotation and deformation of an "agglomerate" made of the original particles held together by a liquid, viscous binder. Results from these simulations yield critical values of the so-called Stokes number (dimensionless parameter of the model containing inertia and viscous dissipation). Below the critical value, the agglomerates are stable and only rotate in response to shear while above the critical value, they break into two or more pieces. At and around the critical value, they attain a steady elongation. These simulation results allow one to obtain correlations of the stable critical versus different parameters of the problem. Comparison with experiments is also shown.

#### 2:15 PM AA2.3

**SOME RHEOLOGICAL BEHAVIORS OF FIBER-LIQUID SYSTEMS.**

Harold Corey, NutraSweet-Kelco Co., Mt. Prospect, IL.

To better understand the flow behavior of fiber-containing food slurries, some aspects of the rheology of such systems was studied using as a model asbestos fiber dispersed in an aqueous medium, 61% sucrose, and in a hydrophobic medium, nujol. Using a coaxial cylinder viscometer, flow curves were obtained at shear rates up to 500 1/sec for five fiber concentrations at temperatures from 10°C. to 50°C. These dispersions are thixotropic and non-Newtonian, their rheology is no doubt a consequence both of fiber-fiber and fiber-liquid interactions. In this paper flow behavior is reported for the upper Newtonian region, beyond 100 1/sec for these systems, where it is assumed the fibers are fully oriented with the flow lines, so that fiber-fiber interactions play only a very minor role. Freed from shear rate dependence, the fiber concentration/viscosity/temperature

relations then presumably arise, in the main, from fiber-liquid interactions.

### 3:00 PM \*AA2.4

THE EFFECT OF SURFACE INTERACTIONS ON THE UNFOLDING AND INTERMOLECULAR ASSOCIATION OF GLOBULAR PROTEINS ADSORBED AT INTERFACES. Sarah Adams, Richard A.L. Jones, Sheffield University, Dept of Physics and Astronomy, Sheffield, UNITED KINGDOM; Rebecca Green, Ian Hopkinson, Cambridge University, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Proteins adsorbed at interfaces are widespread in food systems, where they often play a vital role in providing colloidal stability. The mechanism of colloidal stabilisation and the efficiency in this role depends on the conformation of the adsorbed proteins, which in turn is strongly influenced by their interactions with the interface. We compared the conformational transitions that occur on heating solutions of globular proteins, unfolding and aggregation with the analogous transitions undergone by proteins adsorbed at interfaces. Fourier Transform Infra-red spectrometry in solution and in the attenuated total reflection geometry revealed, for the globular proteins hen-egg lysozyme and bovine serum albumen, both qualitative and quantitative differences between the transitions as they occur in bulk and adsorbed at an interface. In the bulk, unfolding is a sharp transition, followed sequentially on further heating by the relatively sharp onset of the intermolecular association associated with heat set gelation. In contrast, for adsorbed proteins, we found that both processes occur simultaneously over a wide range of temperatures. Proteins were more structurally stable adsorbed at a relatively hydrophilic, solid surface, than at a liquid, hydrophobic surface; in the latter case onset temperatures for both unfolding and intermolecular association were substantially lower than for bulk solutions.

### 3:30 PM AA2.5

ALPHA-LACTALBUMIN SOLUBILIZED IN AOT MICROEMULSIONS UNDERGOES STRUCTURAL CHANGES AND AFFECTS MICROEMULSION PHASE BEHAVIOR. Justin W. Shimek, Catherine M. Pinsky, Stephanie R. Dungan, Univ of California-Davis, Dept of Food Science & Technology and Dept of Chemical Engineering and Materials Science, Davis, CA.

Surfactant stabilized water-in-oil microemulsions spontaneously form and are thermodynamically stable. Protein containing microemulsions show potential for use in separations, biocatalysis, and food or pharmaceutical formulations. Characterization of protein structural changes upon solubilization in microemulsions is key in optimizing extraction methodology and predicting recovered protein functionality. Our objective was to characterize the structural changes of alpha-lactalbumin incorporated into a microemulsion. Conformational changes in alpha-lactalbumin may be related to its unusual effect on the microemulsion phase behavior. Alpha-lactalbumin was allowed to partition into a sodium bis(ethylhexyl) sulfosuccinate (AOT)/water/isooctane microemulsion from an excess aqueous phase and reach transfer equilibrium. The protein conformation and the partitioning of protein, water, isooctane, and surfactant in both the microemulsion and excess aqueous phase were observed as a function of the total protein and surfactant present. Circular dichroism spectroscopy was used to identify changes in protein secondary structure. Protein concentration and water transfer were measured by ultraviolet spectrophotometry and Karl Fischer titration, respectively. Proton NMR measurements provided partitioning information for surfactant and isooctane between the microemulsion and excess aqueous phase. Secondary structure changes of alpha-lactalbumin were observed upon solubilization into the microemulsion and in the excess aqueous phase. Alpha-lactalbumin had a substantial effect on the microemulsion phase behavior. As the total alpha-lactalbumin is increased, there is an initial increase in the water and protein content of the microemulsion phase. As the protein to AOT ratio passes through a critical value, the partitioning of water, protein, and surfactant shifts to the excess aqueous phase. Combining protein structural information with knowledge of the protein, water, and surfactant partitioning a conceptual picture of how the protein interacts with and alters the microemulsion droplet can be developed. Conformational changes in alpha-lactalbumin may allow its incorporation in the surfactant layer of the microemulsion droplet, rather than in the droplet water pool.

## SESSION AA3: IN-ROOM POSTERS

Chair: Jay-Lin Jane

Wednesday Afternoon, December 1, 1999

4:00 P.M.

Falmouth (M)

### AA3.1

PULSED 1H NMR STUDY OF THE HYDRATION BEHAVIOUR

OF VARIOUS STARCH-SUGAR BASED EXTRUDATES.

Carlos W.P. Carvalho, Imad A. Farhat, John R. Mitchell, Nottingham University, Food Sciences Division, Loughborough, UNITED KINGDOM.

Maize grits - sucrose {MG-S} and wheat flour - sucrose {WF-S} mixtures were produced by twin screw extrusion. The amount of sucrose and the extrusion water content varied between 0 and 20% and 14 and 26% {wet basis}, respectively. At constant water and sucrose concentrations, both the degree of starch conversion, specific mechanical energy and sectional expansion achieved varied between systems formulated with maize grits and wheat flour. In order to understand the roles of water and sugars in plasticizing the various biopolymers of these two systems, low field {23 MHz} 1H NMR was used to study the interactions of the various components with water over the water content range between 5% and 35% {dry basis}. These water contents were obtained by storing the extrudates in different RH conditions.

### AA3.2

THE DEFORMATION AND FRACTURE BEHAVIOUR OF AGAROSE GELS IN BOTH TENSION AND COMPRESSION.

Kevin Plucknett, Unilever Research, Colworth Laboratory, Sharnbrook, Bedfordshire, UNITED KINGDOM.

Biopolymer gels such as agar and agarose are promising structuring additives for a number of food applications. Consequently, their large deformation behaviour is of considerable interest. In the current work, the deformation and failure behaviour of agarose biopolymer gels has been assessed in both tension and compression. Failure stress and apparent elastic moduli increased in an essentially linearly manner with increasing biopolymer concentration. Conversely, the failure strain was independent of biopolymer concentration, with compressive failure strains being approximately twice those observed in tension. In addition, the initial elastic moduli were approximately three times greater than the shear moduli, which is consistent with a material with a Poisson ratio of 0.5. Observed stress/strain curves generally showed evidence of strain hardening for all biopolymer concentrations and test conditions, except at the slowest displacement rates (i.e. 5 mm/min), where stress-relaxation occurs within the time scale of the test. These general observations were consistent to other 'brittle' gels. The distribution of measured tensile strengths was found to be suitably described by the Weibull distribution function, which is typically applied to conventional 'brittle' materials such as glasses and ceramics, and the values obtained for agarose gels were comparable to those materials. The influence of agarose gel structure upon failure properties will be discussed.

### AA3.3

CORRELATION OF STRUCTURE AND TEXTURAL INSTABILITY IN INTERMEDIATE-MOISTURE, FLOUR-BASED EXTRUDATES.

Ann Barrett, Nora Beck Tan\*, Paul Maguire, Sustainability Directorate, US Army Soldier Systems Center, Natick, MA; \*Weapons and Materials Research Directorate, US Army Research Laboratory, Aberdeen Proving Grounds, MD.

Flavored flour-based, intermediate-moisture extrudates are under development as jerky-type operational rations, which both simulate a popular military item and provide a source of performance-enhancing carbohydrates. However, these products firm substantially during storage, undermining sensory quality and acceptance. Test extrudates consisting of pure potato flour and potato flour containing 5% of a plasticizer (glycerol, glucose, sucrose or fructose) were produced on a Brabender extruder using a 3mm round die. Samples were placed into accelerated storage at 35°C and withdrawn after 1, 2, and 3 weeks. The effects of the plasticizer type and aging on the extrudates was subsequently evaluated through mechanical testing and x-ray diffraction. Results showed that modulus increased asymptotically for all samples, and after 3 weeks storage was 600-700 percent higher than that for 0-time controls. Each plasticizer at least slightly reduced the degree of firming, with glycerol having the most pronounced effect on texture (17% reduction in average stored modulus). Diffraction spectra for stored samples showed splitting of the broad maxima at 23 degrees, characteristic of all non-stored products, into sharp peaks at approximately 15, 17, 20, and 23 degrees. Results were consistent with published spectra for increasingly hydrated potato starch, indicating movement of moisture from proteinaceous to starch regions in the flour. These results suggest that increased protein association is causative of firming; they furthermore demonstrate that the kinetics of firming may be adjusted through formulation.

### AA3.4

PHASE TRANSITIONS IN TRIGLYCERIDES. Lara Stoimenov, Anthony Robinson, Athene M. Donald, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

Triglycerides are commonly used in many foods, and it is well known

that they are polymorphic. In order to achieve the correct textures, it is important to stabilise the triglyceride in the correct form. Synchrotron radiation has been used to study phase transitions in several different triglyceride systems during controlled thermal histories. For the case of cocoa butter, which contains several related triglycerides with slightly different chemistries, it appears that phase segregation of the components may occur. This may have significant implications for the behaviour of cocoa butter in confectionery according to its processing history. Other triglycerides are also subject to instabilities during storage, again with significant implications for their use.

#### **AA3.5**

**THE CONFORMATIONAL RESPONSE OF GUAR GALACTOMANNAN TO DIFFERENT SALT ENVIRONMENTS.** M.R. Gittings, M. In, C. Marques, Rhodia/CNRS Joint Laboratory, Rhodia Inc., Cranbury, NJ; J. Lal, IPNS, Argonne National Laboratory, Argonne, IL; L. Cipelletti, V. Trappe, D. Weitz, Dept. of Physics, Univ. of Pennsylvania, Philadelphia, PA.

Guar is a naturally occurring polysaccharide known mostly for its ability to noticeably increase solution viscosity at relatively low concentrations. Randomly distributed galactose units along a mannose backbone insure good polymer solubility in water through steric effects. However, it is believed that the random nature of the substitution leads to inter- and intrachain associations through the guar chain segments which are galactose-poor. These associated regions have important consequences for the structure of the chains and for the physical behavior of the solution. Despite its widespread use, very little is known about the conformation of guar in solution and the response of the chains to varying solvent conditions. It is well-known that certain ions are more effective than others at reducing the solubility of some water-soluble molecules (the Hofmeister effect). The conformation of guar in the presence of four different salts is presented. The data were collected using light and neutron scattering and cover a wide q-range.

#### **SESSION AA4:**

Chair: Michael J. Gidley  
Thursday Morning, December 2, 1999  
Provincetown/Orleans (M)

#### **8:30 AM \*AA4.1**

**CREATING NEW STARCHES.** Alison M. Smith, John Innes Centre, Norwich, UNITED KINGDOM.

I shall discuss the extent to which the properties of starch can be altered by manipulation of the enzymes responsible for its synthesis in the plant. The two main enzymes involved in the synthesis of starch polymers from ADP glucose - starch synthase and starch-branching enzyme - are present in plants as multiple isoforms, each of which displays distinct properties. Studies of the starch of mutant plants in which particular isoforms are missing, and genetically manipulated plants in which the contribution of particular isoforms has been selectively reduced, reveal that each isoform plays a unique role in determining the structure of the starch polymers and hence the properties of the starch. The precise contribution of a particular isoform is dependent not only on its intrinsic properties but also upon the complement of other isoforms present in the plant. The great complexity of the process of starch synthesis makes it difficult to 'design' starches with specific, desirable physical properties by manipulating the complement of isoforms of the enzymes in the plant, but also allows a wide range of different starch properties to be generated by this means.

#### **9:00 AM AA4.2**

**HIGH AMYLOSE POTATO STARCH: PRODUCTION AND GELATINISATION PROPERTIES.** Mike Gidley, Martine Debet, Gerhard Schwall and Steve Jobling, Unilever Research, Colworth House, Sharnbrook, Bedford, UNITED KINGDOM.

Gene technology has the potential to expand the range of ingredients and components available to the food industry, by providing molecular compositions not currently available at commercial scale. One such possibility is that of a high amylose potato starch. Although high amylose variants of many starch-producing plants are available (e.g. corn, barley, pea), none had previously been described for potato. Through the down-regulation of two isoforms of starch branching enzyme, it has been possible to generate potato plants with starch having more than twice the usual level of amylose. This has a profound impact on swelling and gelatinisation properties, opening up a wider range of properties than had previously been obtainable from potato starch.

#### **9:15 AM AA4.3**

**SCATTERING STUDIES TO UNRAVEL STARCH GRANULE STRUCTURE.** Paul A. Perry, Thomas A. Waigh, K. Lisa Kato, Sue Robinson, Athene M. Donald, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

X-ray scattering has been used to probe variations between species in the structure of the native starch granule, and how this structure breaks down during processing. Microfocus X-ray techniques allow local orientation variations within a single granule to be observed. Small angle scattering explores how longer range correlations are affected by both temperature and the presence of solvent. Systematic changes can be found in different structural parameters between different species and cultivars. An ultimate aim is to relate these changes in packing to the genes involved in the enzymes involved in the starch synthesis.

#### **9:30 AM AA4.4**

**EFFECTS OF AMYLOPECTIN BRANCH-LINKAGE STRUCTURES ON PROPERTIES OF STARCH.** Jay-Lin Jane, Department of Food Science and Human Nutrition, Iowa State University, IA.

Native starches that display A- and B-type crystallinities show different arrangements of branch linkages in their amylopectins. A-type starches have branch-linkages scattered between amorphous and crystalline regions, whereas B-type starches have branch-linkages clustered in the amorphous region. A-type starches are susceptible to enzyme hydrolysis, whereas B-type starches are resistant. Starches that have fewer branch chains with 17-21 glucose units (shown as a shoulder on the branch chain-length distribution) generally display lower gelatinization temperatures. The distances of the chains are in the vicinity of the length of starch crystalline region, 6.65nm, reported by Donald and co-workers.

#### **9:45 AM AA4.5**

**THE MATERIAL PROPERTIES OF STARCH-MODIFIED TRANSGENIC POTATOES.** Andrew Ormerod, Julie Ralfs, Mike Gidley, Unilever Research Colworth, Sharnbrook, Beds, UNITED KINGDOM.

Potatoes have a wide number of applications within the food industry and yet the mechanism by which softening occurs on heating is not clearly understood. The application of heat to potato tuber parenchyma tissue results in two independent events; weakening of the binding between the cells and gelatinisation and swelling of the intra-cellular starch. The concurrent nature of these processes has meant that in the past it has not been possible to establish their individual contribution to the separation of cells, which leads to the softened texture of cooked potato tissue. Potato plants containing starches with high amylose contents and consequently reduced swelling properties were developed. These modified starch properties provided the opportunity to separate cooking effects of the middle lamella pectin from the swelling of the starch, by studying the influence of heat on the material properties of a range of starch-modified transgenic potatoes. Four lines of potato were studied; three with the starch being composed of increased proportions of amylose and a control. The strength of the heated tissue decreased markedly following thirty minutes at 80C or five minutes at 100C. Microscopy indicated that starch swelling decreased as the amylose level increased for the same thermal treatment. All the lines followed the same trends with regard to the thermal weakening of the tissue. Microscopy of the line in which there was minimal starch swelling, indicated that the cells of the cooked tissue principally contained fluid, in contrast to the controls in which the cells were filled with swollen starch on cooking. Therefore, we conclude that the weakening of the potato tissue is primarily controlled by the thermal degradation of the middle lamella.

#### **10:30 AM \*AA4.6**

**STARCH STRUCTURE-FUNCTION RELATIONSHIPS - FROM THE LAB TO THE REAL WORLD.** Louise Slade, Harry Levine, Nabisco Research, East Hanover, NJ.

At numerous conferences since 1982, we have presented results of our work on starch structure-function relationships, based on our food polymer science approach to studies of starch gelatinization, retrogradation, and annealing. We've used laboratory measurements, frequently made on experimental, benchtop model systems, to gain insights and increased understanding of starch-based ingredients, products, and processes. In real world industrial manufacturing settings, such starch-containing systems exist in time-dependent physical states far from equilibrium, where the kinetics of state transitions (e.g. the glass transition that controls gelatinization, retrogradation, and annealing), as influenced by plasticization by water and temperature (the effects of which are best illustrated by means of state diagrams), are more practical, relevant and informative than are theoretical considerations of equilibrium thermodynamic

phases. In this talk, we'll present material selected from among our recent studies on starch structure-function relationships, as related to cooking of whole-kernel corn for masa production, value-added processing of rice starches, flours and grains, functionality of potato and waxy maize starch ingredients in chip-like baked snacks, wheat starch gelatinization during cookie baking and retrogradation during shelf-life, and oil-roasting.

**11:00 AM AA4.7**

**EFFECTS OF ULTRA PRESSURE TREATMENTS ON THE CRYSTALLINE STRUCTURES OF STARCH GRANULES.** Herman Katopo, Kit-Sum Wong, Andrew E. McPherson, Jay-lin Jane, Department of Food Science and Human Nutrition, Iowa State University, Ames, IA.

Native starches display various x-ray diffraction patterns, which are categorized to A-, B-, and C-types. X-ray patterns of starches relate to the branch chain-length and the branch-linkage locations of amylopectin. The branch chain-length distributions and branch-linkage locations also determine the gelatinization temperature, enzyme digestibility, and surface pin-holes of starch granules. It is known that starches displaying the A-type x-ray pattern have shorter branch chain-length, with branch-linkages scattered in the crystalline and amorphous regions, and are more easily digestible by enzymes. In contrast, starches of the B-type pattern possess longer average chain-lengths, with branch-linkages mostly clustered in the amorphous region, and are more resistant to enzyme hydrolysis. Starches of the B-type pattern have loosely-packed crystalline structures, which consist of about 36 water molecules in each unit cell. B-type starches can be partially converted to the A-type by high-temperature/moisture treatments, but not the A-type starches. By using an ultra-pressure treatment at 690MPa, ambient temperature, and with water presence, we have observed that the A-type starches are converted to the B-type, whereas the B-type starches remained unchanged. The differences may be attributed to the branch structures of the amylopectins. The B-type starches, with long branch-chains and the branch-linkages clustered in the amorphous region, are more difficult for branch-chain rearrangement. The pressure-treated starches displayed pasting properties resembling that of cross-linked starches.

**11:15 AM \*AA4.8**

**MOBILITY CHARACTERIZATION OF HYDRATED STARCH USING NMR AS RELATED TO GLASSY-RUBBERY TRANSITION.** Yang Kou, Pavinee Chinachoti, Dept of Food Science, Univ of Massachusetts, Amherst, MA.

Plasticization of starch systems was studied by the mechanical relaxation and Nuclear Magnetic Resonance (NMR) spectroscopy. Relationships between the mechanical and molecular relaxation dynamics (e.g., water) will be discussed. The summarized results on solid state NMR investigation over a moisture and temperature range revealed a discrepancy between the long-range glass transition and short-range molecular water mobility. Hydrated wheat starch was studied by carbon-13 CP/MAS and wide-line 1H NMR changing in intensity with moisture content and temperature indicating carbon chain mobility change. However, T1rho(1H) values (based on single exponential model) failed to show any indication of mobility change vary significantly over a 2-11% moisture for waxy corn starch and over 0-60C for wheat starch. Broad and narrow component T2\* (from linewidth) and narrow T2 (CPMG) indicated a decrease in mobility with increasing solid concentration with a 'break point' at 20-22% water content. T1 minimum was observed also at the same concentration. Water molecules remained very high in mobility regardless of the relative rigid starch molecules in the glassy state.

**11:45 AM AA4.9**

**PULSED MAGNETIC FIELD CONTROLLED ENZYMIC PROCESSES IN FOOD INDUSTRY.** Mark N. Levin, Voronezh State University, Nuclear Phys. Dept, RUSSIA; Ludmila V. Antipova and Irina A. Glotova, Voronezh State Technological Academy, Dept of Meat Production and Meat Products, RUSSIA.

Biocatalytic processes and treatments become widely used in technology of food industry nowadays. In this report we present an effective method of controlling the enzymatic processes and treatments by pulsed magnetic fields (PMF). The method is based on the recently revealed possibility of relatively weak (<1 T) PMF to change activity of enzymes and kinetics of the enzymatic reactions. Effect of long-time (tens of hours) changes of activity of extracted enzymes after the short-time (several seconds) PMF treatment is presented for the first time. The effect is caused by conformation changes of the enzymes due to breaking of hydrogen bonds in their secondary structure by the PMF. The other effect, namely PMF influence on kinetics of enzymatic reactions, takes place at the stage of formation of intermediate enzyme-substrate complexes, which represent themselves spin-correlated radical pairs. Physical

mechanisms of the both effects are given. High sensitivity of the effects to the PMF parameters allows one both to activate and to suppress enzymatic processes. Of great importance is the possibility of selective activation (or suppression) of individual enzymes in complexes. The stimulating effect of the PMF-treatment was successfully demonstrated in preparing high-quality meat products, formatting collagen substances with controlled properties, accelerating cultivation of mycelium, increasing extra-activity of malt, activating of seeds before sowing etc. The suppressing effect of the PMF-treatment was effectively used for stabilization of food products quality at storage. The relevant biochemical mechanisms of the PMF-controlled processes are considered.

**SESSION AA5:**

Chair: Richard A.L. Jones  
Thursday Afternoon, December 2, 1999  
Provincetown/Orleans (M)

**1:30 PM AA5.1**

**THE PROCESSING OF SOFT CHEESE: RELATIONSHIP BETWEEN PROCESS HISTORY AND PRODUCT STRUCTURE.** Carole AF Dupont, Lynn F. Gladden<sup>†</sup> and Peter J. Fryer<sup>\*</sup>, Unilever Research, Colworth House, Sharnbrook, Bedford, UNITED KINGDOM, <sup>†</sup>Dept. of Chemical Engineering, University of Cambridge, UNITED KINGDOM; <sup>\*</sup>School of Chemical Engineering, University of Birmingham.

Cheese has a complex structure which controls its material properties and thus consumer qualities: the same material can make hard (parmesan) and soft (cottage) cheeses, depending on moisture content and history. The aim of this work was to relate the process history of a soft cheese to its final rheological properties. Systematic experiments were undertaken to develop a processing route which was quantified in an engineering sense; in which the shear-temperature-time history was known. Experiments then studied the behaviour of the material as a function of the process history; it proved possible to correlate the strength of the final product with the degree of denaturation of the proteins in the cheese matrix. Micrographs of the structure of cheese were studied using image analysis and relationships between the fractal dimension of the structure and the process history identified. The work demonstrates how materials science techniques can be applied to such materials; however, the complexity of the chemistry of the system makes the prediction of quality difficult.

**1:45 PM AA5.2**

**MECHANISMS OF PHASE SEPARATION IN GELLING BIOPOLYMER MIXTURES.** R.A.L. Jones, Department of Physics and Astronomy, University of Sheffield, Hicks Building, Sheffield, UNITED KINGDOM.

Mixtures of biopolymers often contain at least one component that can physically gel, so the morphologies that result when these mixtures phase separate arise from the competition between phase separation and gelation. The interaction between these two processes results in a very rich range of possible morphologies. We have studied such morphologies in mixtures of gelatin and dextran. Our experiments are done both in real space, using confocal microscopy, and in reciprocal space, using time-dependent light scattering experiments. Confocal microscopy is particularly powerful in elucidating the connectivity of the phases, which largely controls the rheological properties of the mixture, while light scattering permits a quantitative analysis of the phase separation mechanism in terms of classical theories such as the Cahn linear theory of spinodal decomposition.

**2:00 PM \*AA5.3**

**BREAKDOWN AND RHEOLOGY OF FOOD IN THE MOUTH.** Peter Lillford, Unilever Research, Colworth House, Sharnbrook, Bedfordshire, ENGLAND.

The origin of perceived textural attributes of food in the mouth is not well understood. Early work successfully identified the initially perceived properties with the modulus, elasticity and fracture properties of the whole food piece. However, it soon became apparent that discriminating attributes were associated with the whole process of breakdown during chewing and could not be described by or associated with the initial food structure. Attempts to understand in-mouth breakdown by experimentation observation; construction of mouth analogue devices and mathematical simulation will be described for both solid and liquid foods. Attention will be drawn to the significance of early training which relates breakdown pathways and perception to final product preference.

**2:30 PM AA5.4**

**A RANDOM SQUEEZE TECHNIQUE FOR THE**

**DETERMINATION OF THE VISCO-ELASTIC PROPERTIES OF FOODSTUFFS.** Anthony C. Fischer-Cripps, John S. Field, Bruno Pfister, CSIRO Division of Telecommunications and Industrial Physics, Sydney, AUSTRALIA; Geoffrey W. Francis, Sonya Huang, Food Science Australia, Sydney, AUSTRALIA.

A method of rapidly determining the complex modulus of foodstuffs over two decades of frequency is described. The method utilizes random squeezing with Fourier analysis to provide the complex modulus as a function of frequency and time. The method uses very small displacements, and requires only a few millilitres of sample volume. Application of the method to the food industry allows subjective mouth feel tests to be quantified and also to provide information for the purpose of optimizing of food processing procedures.

**2:45 PM AA5.5**

**STUDIES OF BIOPOLYMER GELATION UNDER SHEAR.** Bronwyn L. Elliot, School of Chemical Engineering, University of Birmingham, UNITED KINGDOM.

Biopolymer sheared gels from polysaccharides such as agars, carrageenans and alginates provide the food industry with new opportunities for structuring foods and making foods with novel properties. The application of sheared gels will be facilitated if it is possible to predict the development of shear gel microstructure as a function of process conditions, such as shear rate, biopolymer concentration and cooling rate). The ultimate aim is to control the microstructure of the material as a function of the applied process conditions and to provide a bases for improved structure control. Sheared gel technology produces a suspension of microgel particles rather than a solid mass. The gel is liquid like and consists of a matrix of polymer rich particles surrounded by a polymer depleted liquid. Structural properties of the final gels have been characterised by techniques such as rheology and microscopy and modelled using simple rheological expressions which give information about flow properties of the material but this does not enable the prediction of structure formation. Fluid gels are thought to form when shear disrupts the quiescent gelation mechanism at the gelation point to produce particles. Since the quiescent gel mechanism is still not completely understood it is unclear if the sheared gel particles form as a result of, shear breaking the critically branched quiescent gel structure, nucleation and growth of particles under shear or if shear changes the processing environment so that particles form as a result of phase separation/spinodal decomposition mechanism. This work examines these underlying mechanisms relating to the formation of a sheared gel, the composition of the sheared gel phases and their relationship to microstructure.

**3:30 PM AA5.6**

**MECHANICAL BEHAVIOUR OF EDIBLE FILMS.** Mats Stading, Martin Anker, Anne-Marie Hermansson, Chalmers University of Technology and SIK-The Swedish Institute for Food and Biotechnology, Gothenburg, SWEDEN.

Films of biopolymers such as polysaccharides, proteins and lipids have many potential uses in food applications. Free-standing biopolymer films for packaging use were already developed during the fifties but were driven out of competition by plastics. Biopolymer based films are again considered as alternatives to plastics due to environmental concerns. Packaging solutions based on materials from renewable resources gives no net increase of atmospheric carbon dioxide and biopolymers are mostly degradable facilitating closed waste management systems. Edible biopolymers can be applied directly on foods to give new solutions for prolonged shelf-life as alternative to conventional packaging. An edible coating is either consumed with the product or disappears during processing. Internal migration of moisture or fat in, especially prefabricated foods, decreases quality and shelf-life. An edible barrier between the different components of the food product can prevent this. The mechanical and barrier properties of biopolymer films are strongly dependent on the microstructure. We have studied solution-gel-cast films based on potato starch and whey protein to elucidate this dependence. Films of native starch, pure amylose and pure amylopectin have been shown to behave differently in respect to barrier and mechanical properties. Amylose forms strong films with constant relative crystallinity whereas amylopectin forms films of varying crystallinity depending on the humidity conditions during formation. The humidity conditions during formation of amylose films also influence the properties, which was related to the microstructure rather than the crystallinity. The effect of the biopolymer network was studied in whey protein films. The protein concentration was varied around the critical concentration needed to form the network in the gel state. The film strength did not increase uniformly with increasing protein concentration, instead a maximum was found. The existence of a maximum was attributed to a change in the protein network structure.

**3:45 PM AA5.7**

**THE FRACTURE BEHAVIOUR OF MIXED BIOPOLYMER GEL COMPOSITES.** Kevin Plucknett, Valery Normand, Stephen Pomfret, Dudley Ferdinando, Unilever Research, Colworth Laboratory, Sharnbrook, Bedfordshire, UNITED KINGDOM.

Mixed biopolymer gels are promising structuring additives for a number of food applications and, as a consequence, it is important that their large deformation behaviour is well understood. In the present work, the deformation and failure response of biopolymer gel composites, comprised of a mixture of gelatin and maltodextrin, have been assessed in both tension and compression. When mixed in solution, and then gelled, this biopolymer system phase separates to give a structure in which one biopolymer is continuous while the other forms discrete spherical inclusions. Small amounts of each biopolymer partition into the other during this process, in line with phase diagram considerations. When the maltodextrin-rich phase is continuous, the mixed gels are 'brittle', deforming in a linear elastic manner up to failure. Conversely, when the gelatin-rich phase is continuous the gels exhibit a 'pseudo-yielding' behaviour, similar to many plastic and metallic materials. Tension and compression tests performed dynamically on a confocal laser scanning microscope (CLSM) demonstrate that this 'yielding' phenomenon is due to progressive debonding of the interface between the two phases. During cyclic tests, where samples are unloaded prior to failure, it is observed that the apparent plastic deformation is partially (but not completely) recoverable. Initial calculations indicate an interfacial fracture energy of  $\sim 0.25 \text{ J/m}^2$  for this system, comparable to glassy polymer interfaces. Potential application of the 'Essential Work of Fracture' concept to these composite gels, in order to determine the relative elastic and plastic contributions to deformation, will also be discussed.

**4:00 PM AA5.8**

**RELATING MICROSTRUCTURE TO THE MECHANICAL PROPERTIES OF ICE CREAM: CRITERIA FOR MICROSTRUCTURAL CHARACTERISATION.** Paul A. Trusty, Mark Kirkland, Iain Campbell, Unilever Research, Colworth House, Sharnbrook, Bedfordshire, UNITED KINGDOM.

A materials science approach has been used to assess the microstructure-property relationships in aerated ice creams. Mechanical property data were measured using the 3-point bend test which involved bending moulded bars of set dimensions to failure whilst recording the corresponding force-displacement curves. The shape of the force displacement curve was found to give clues as to the way in which the ice cream fractured on a microstructural level. Predicting the mechanical properties of ice cream from its microstructure is made extremely difficult, however, by the complexity of the material, which is a four phase system of ice, air, fat and matrix and exhibits composite behaviour on a microscopic scale. Cryogenic scanning electron microscopy (SEM) has been used to visualise a range of ice cream microstructures which have been characterised subsequently using stereological parameters. This work raises issues on the development of microstructure-property relationships in ice cream by showing that the selection and measurement of relevant ice cream microstructural parameters must be coupled with an appreciation of the dependence of the measured mechanical properties on these parameters.

**4:15 PM AA5.9**

**DEFORMATION OF CELLULAR SYSTEMS.** Debbie J. Stokes, Bradley L. Thiel, Athene M. Donald, Cavendish Laboratory, University of Cambridge, UNITED KINGDOM.

Environmental Scanning Electron Microscopy (ESEM) permits hydrated samples to be imaged in their natural state, and without the need for coating of the sample. This means it is ideal for carrying out in situ deformation experiments on cellular foods such as vegetables and breadcrumbs, imaging and simultaneously recording the load-extension curve. Results will be presented for the compression of carrot parenchyma tissue, showing how age and cooking history affect the mechanism of deformation. The turgor pressure in the cells is a key parameter, but cooking also affects the cell wall properties. Data will also be shown for breadcrumbs hydrated to different extents. As the degree of plasticisation increases, the modulus drops and more of the deformation is recoverable.

**4:30 PM AA5.10**

**INVESTIGATIONS INTO THE INFLUENCE OF PARTICLE SIZE OF MICROGEL SPHERES UPON THE MATERIAL PROPERTIES OF MODEL BIOPOLYMER GEL COMPOSITES.** Stephen Pomfret, Theo Blijdenstein, Valery Normand, Kevin Plucknett, William Frith, Unilever Research, Colworth Laboratory, Sharnbrook, Bedfordshire, UNITED KINGDOM.

The large deformation material properties of some model composite biopolymer gel systems have been investigated using mechanical

testing and confocal laser scanning microscopy. Samples were prepared by dispersing spherical biopolymer microgel particles (20-200 microns) in gelatin solutions, which were subsequently allowed to gel. This resulted in the formation of mixed gel composite systems having an included phase of known volume fraction and well defined particle size. Compression and tension tests were performed upon a range of samples having varying particle radii, and the trends in material properties noted. Confocal laser scanning microscopy of composite samples under varying degrees of applied strain was used to observe debonding of the matrix from the surface of the particles, and to monitor this process as a function of particle size.