Experiments and Models for Polymeric Microsphere Foams

Final Report

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Summary of the Project Report: NCC-1-02003

The current project was performed under the direction of Dr. Byron Pipes as its lead investigator from January 2001 to August 2004. With the permission of the NASA, the project was transferred to Dr. Thein Kyu as the principle investigator for the period of September 2004 - June 2005. There were two major thrust areas in the original proposal; (1) experimental characterization and kinematics of foam structure formation and (2) determination of the mechanical, physical, and thermal properties, although these thrust areas were further sub-divided into 7 tasks. The present project has been directed primarily to elucidate kinematics of micro-foam formation (tasks 1 and 3) and to characterize micro-foam structures, since the control of the micro-structure of these foams is of paramount importance in determining their physical, mechanical and thermal properties. The first thrust area was accomplished in a timely manner; however, the second thrust area of foam properties (tasks 2, 4-7) has yet to be completed because the area of kinematics of foam structure formation turned out to be extremely complex and thus consumed more time than what have been anticipated. As will be reported in what follows, the present studies have greatly enhances the in-depth understanding of mechanisms and kinematics of the micro-foam formation from solid powders. However, in order to implement all objectives of the second thrust areas regarding investigations of mechanical, physical, and thermal properties and establishment of the correlation of structure – properties of the foams, the project needs additional time and resources.

The technical highlights of the accomplishment are summarized as follows. The present study represents a first approach to understanding the complexities that act together in the powder foaming process to achieve the successful inflation of polyimide microstructures. This type of study is novel as no prior work had dissected the fundamentals that govern the inflation process in this type of systems. The systematic approach to each of the different phenomena (i.e. morphological, diffusive, kinetic and dynamic) brings into context each of them in a way that allows separate understanding and analysis. Of the different phenomena studied, probably the one that gives a higher level of control over the inflation process has been shown to be the morphological aspects of the precursor particles. It is a major contribution of the present work to isolate and identify this phenomenon and highlight the features that with careful control during the synthesis of the precursor material can lead to a highly optimized and specialized final product (neat foam or microstructure). Some of these accomplishments have been presented in various national meetings and some of which are either published in refereed journals or still in various stages of publications. One of the presentations was selected for "Best of ANTEC 2004" Online Presentation Series of the Society of Plastics Engineers (SPE) (September 2004) (http://members.4spe.org/eLearning/courseDescription.cfm?cid=149).

1. Objectives of the Original Proposed Studies (Presented in an unsolicited research proposal 08/13/01)

1.1. Microsphere Kinematics – Experiments and Models

The understanding of the kinetics of polyimide hollow microsphere formation, growth and deterioration requires that models be developed for the characteristics of the blowing agents, sphere inflation kinetics, polymer property development with thermal cycle, diffusion of blowing agent through the polymeric sphere wall and the joining of these models to yield an understanding of foam performance.

1.1.1 Blowing agent properties

It is essential to develop the relationships between temperature and the pressure developed by the blowing agent. Both rate and magnitude of temperature are presumed to influence the blowing agent for a given polymer system.

1.1.2. Sphere inflation kinetics

The kinetics of the sphere inflation from its initiation as a micro particle to its full inflation must be modeled in a manner that captures the radial growth of the sphere as a function of temperature and time. Polymer particle size distribution and blowing agent characteristics as a function of temperature must be included in the analysis.

1.1.3 Polymer properties versus time-temperature

The polymer properties including viscosity, thermal conductivity, blowing agent diffusion rate constant and the molecular weight gain must be modeled as a function of temperature. It is also necessary to characterize and model the viscoelastic properties of the polymer.

1.1.4 Sphere size versus time-temperature

The above models will be integrated into a single model that predicts microsphere behavior for initiation to inflation and growth and finally to the molecular weight gain rupture. Experiments will be carried out to verify the models of microsphere growth.

1.2. Microsphere Properties – Experiments and Models

The elastic properties of microspheres will determine the corresponding properties of foams produced from them. The above-described models can be used to predict a range in possible mechanical properties based on polymer properties and microsphere geometries.

1.2.1 Elastic properties

The elastic properties of the microsphere can be predicted for multiple polyimide polymers and multiple geometries (diameter and wall thickness).

1.2.2 Viscoelastic properties

The viscoelastic properties of the microsphere will correspond to the viscoelastic properties of the polyimide polymer. Time-dependent behavior must be predicted and measured.

1.2.3 Burst and crushing strengths

The burst and compression strengths must be measured under controlled conditions. For crushing strength, the test conditions will likely require a multiple sphere interaction geometry. Burst can be evaluated in high vacuum with low wall thickness or at elevated temperature.

1.2.4 Diffusion properties

The diffusion properties of the sphere must be measured not only for the blowing agent, but also for air, moisture, hydrogen and oxygen.

1.2.5 Thermal conduction properties

The thermal conduction properties of the microsphere must be modeled and measured to develop an understanding of their properties as insulating foam. Initial results will focus on performance of individual microsphere.

1.3. Foam Geometries – Experiments and Models

Foam geometries that result from both microsphere and friable balloons must be studied experimentally in order to relate cell geometry, cell size, wall thickness and cell anisotropy to the foam generation process and the precursor geometry and cure state.

1.3.1 Cell geometries

Cell geometry is likely a function of precursor geometry, polymer blowing agent, state of polymerization and thermal cycle. These variables must be studied experimentally and utilized to guide foam model development.

1.3.2 Cell size and wall thickness

The cell size and wall thickness will likely influence the mechanical properties, thermal conductivity and diffusion properties of the foam.

1.3.3 Cell Anisotropy

The cell anisotropy may strongly influence the mechanical properties of the foam. It must be measured and considered in the foam model development.

1.4. Foam Mechanical Properties – Experiments and Models

The mechanical properties of the foam must be measured and compared to theoretical predictions. Compressive strength, shearing strength and tensile strength may or may not be intrinsic and therefore independent of geometry. Experimental efforts must be undertaken to answer this question.

1.4.1 Compressive properties

The compressive strength is determined by microinstability of the cell walls. Models are available in the cellular materials literature. These must be exercised and evaluated for predicting foam compressive strength. Experiments must be carried at the macro and micro levels to develop an understanding of compressive strength.

1.4.2 Shearing properties

The shearing strength of polymeric foam is extraordinarily important in determining the potential for use as core in sandwich structures. Shearing strength may be controlled by tensile and/or compressive strength of the foam. Test methods must be developed and interpreted to establish intrinsic shearing strengths and modulus.

1.4.3 Tensile strength

The tensile strength and modulus of a polymeric foam can also be modeled with theories from the cellular materials field. Fracture and crack propagation are potential failure mechanisms. In addition, defects in the cell structure may provide the dominant mechanism for failure. Test methods are particularly sensitive to specimen geometry. Both macro and micro tests must be conducted.

1.5. Foam Thermal Properties – Experiments and Models

The thermal properties of polymeric foams provide one of their primary benefits as thermal barriers. The heat transfer characteristics of the foam cell are determined by its geometry and material properties. Closed cell and open cell geometries will yield significantly different properties. From the results for the microsphere it should be possible to estimate the properties for closed cell foams. Open cell foams must be modeled as a combination of unit cell and open passageways. Tests must be carried out at the macro and micro levels. Further, the combustion characteristics are influenced by the properties of the polymeric materials and the foam cell geometry. These issues must be combined to predict foam flammability.

1.5.1 Thermal conductivity

The thermal conductivity of the foam must be predicted from the unit cell analyses. Anisotropy in thermal conductivity will likely follow from geometric anisotropy of the foam. Tests at the micro and macro levels must be carried out.

1.5.2 Combustion characteristics

The combustion characteristics of the foam must be modeled as a function of polymer properties and cell geometry. Tests at the macro and micro levels are required.

1.6. Foam Diffusion Properties – Experiments and Models

The diffusion of gases through the foam will be a function of polymer properties and cell geometry. Even for closed cell geometries gases can diffuse through the cell walls and penetrate the foam. These properties are particularly important at cryogenic conditions. Macro and micro experiments must be carried out.

1.6.1 Open cell vs. closed cell

The degree of openness of the cell structure must be determined and predicted for the foam if it is to be optimized for thermal and diffusion properties. Percolation theory may provide a foundation for prediction of these properties. Macro and micro experiments are necessary.

1.6.2 Gas and liquid phase: hydrogen, nitrogen, water vapor

Gas phase diffusion in foams for water vapor, hydrogen and oxygen are important to understand the phenomenon of "cryopumping". Here cyclical thermal environments can lead to destruction of the foam or face sheets when phase change of the hydrogen or oxygen occurs. Modeling and experiments must be undertaken to clarify these phenomena.

1.7. Functionally Gradient Foams – Experiments and Models

The development of foam microstructure from homogeneous polymer precursor will likely produce uniform properties through the thickness. Functionally gradient materials is a concept developed for powder metals and ceramics that allows for the "design" of material property gradients that provide more optimum performance. These concepts can also be applied to polymeric foams.

1.7.1 Gradient in sphere diameter

Control of the distribution of sphere or cell diameter through the thickness of the foam is the first obvious functionally gradient material to evaluate.

1.7.2 Gradient in wall thickness

Gradients in cell wall thickness through the thickness might provide more optimum mechanical and thermal properties.

1.7.3 Gradient in polymer composition

Perhaps the most exciting possibility is a functional gradient in polymer properties. Here the properties can be varied through the thickness to yield optimum solutions.

1.7.4 Mixtures

Mixtures of microspheres, balloons, polymer powder and different polymers will allow for the generation of "alloys" of foams with the corresponding range in properties.

2. Research Accomplishments

One graduate student, Mr. Camilo Cano, defended successfully his Ph.D. dissertation on July 11th of 2005 before a faculty committee at The University of Akron and graduated on 08/27/05. The accomplishment of his dissertation research is compiled under the title of "Polyimide Microstructures from Powdered Precursors: Phenomenological and Parametric Studies on Particle Inflation". An abstract of this dissertation is presented below:

- 2.1 Abstract of Ph. D. Dissertation of C.I. Cano:

  Polyimide foams have emerged as a high performance cellular materials with great potential for applications in aerospace due to their excellent mechanical, chemical and electrical properties. A novel technology in the development of polyimide foams consists of a solid precursor in the form of a powder with an embedded blowing agent that can be converted by simple thermal treatment into single polymeric spherical microstructures or inflated together to produce foams with varying ranges of density and properties. This technology is hereafter referred to as solid-state powder foaming.

Solid-state foaming from poly(amic acid) precursor particles was studied by examining concurrent and competitive phenomena that determine the morphology and physical properties of the resulting polyimide microstructures. Phenomenological analysis of morphological relations, as well as physicochemical processes provided a comprehensive understanding of the governing principles by which potential particle inflation is achieved. The resulting polyimide microstructures present morphologies that are the result of the combined effect of morphological features on the precursor particles, blowing agent concentration and processing conditions exerted on the powders during the inflation process. A strong interrelation was found between different controlling factors such as precursor morphology and processing conditions. The balance between local temperature and concentration inside the particles can be manipulated by these controlling factors in such way that a particle under a certain set of conditions might experience multiple bubble growth, while under slightly different conditions might present single bubble inflation or no inflation at all.

The results from the phenomenological analysis served as the basis of a numerical model and corresponding parametric study where the different parameters of the governing phenomena were evaluated and studied. This parametric study provided a comprehensive understanding of the interrelation of the different parameters and conditions which govern the inflation of powdered precursors. By having separated each of the different phenomena, as well as their sources and effects, future research in the field of powder foaming can center on specific issues where optimization or fundamental understanding is required. The comprehensive understanding hitherto achieved from the present work lays the groundwork for further optimization of the powder foaming process towards better control of foam properties and novel application development.

Along with the study of the aforementioned phenomena, a complete review of fundamental topics which have bearing on the understanding of the different physical and chemical principles involved was presented. This review will serve as a bibliographical tool for future research on the topic of foaming in general and polyimide cellular structures in particular. Finally, the fact that future studies on the foaming of powdered systems will have a clearly defined set of research fields to continue from is in itself a contribution to the advancement of science and engineering in the field of high performance cellular materials.

3. Refereed Publications

- 3.1. C. I. Cano, E. S. Weiser and R. B. Pipes "Solid-State Polyimide Foaming from Powder Precursors: Effect of Morphology and Process Parameters on the Diffusive Phenomena," *Cellular Polymers*, 23, 5 (2004) p.299.

  Abstract:

  Solid poly(amic acid) (PAA) precursor is used for foaming into microspheres or foams depending on whether the powder particles are free or confined inside a mold.

Solid-state foaming of powder precursors is studied by examining concurrent and competitive phenomena that determine the morphology and physical properties of the foam unit cell. Simultaneous analysis through thermo gravimetric analysis (TGA) and modulated differential scanning calorimetry (MDSC) is proposed for the characterization of important transitions during the blowing process. Effects of particle size and shape on bubble growth will be addressed.

- 3.2. C.I. Cano, E.S. Weiser, T. Kyu and R. B. Pipes "Polyimide Foams from Powder: Experimental Analysis on Competitive Diffusion Phenomena," accepted for publication in *Polymer* (July of 2005).

  Abstract:

  In the present study, various diffusive processes have been investigated during foaming of powdered precursors of polyimide. A detailed analysis of the powdered precursor's characteristics allows for an enhanced morphological understanding of the resulting microstructures and foam unit cell. Parameters that are central to the foaming process such as particle morphology, volatile concentration and sorption-desorption processes are evaluated. Isothermal and non-isothermal desorption experiments have been carried out by thermogravimetric analysis (TGA), and specific diffusive processes have been correlated to thermodynamic and kinetic transitions by means of modulated differential scanning calorimetry (MDSC) of the corresponding materials. It was found that two primary fluxes of volatiles, one out of the external surface of the particles (responsible for volatile desorption) and the other into the growing bubble (responsible for vapor supersaturation inside the bubble) compete against each other creating a competitive scenario that becomes the controlling factor for potential inflation within the precursor particles.

4. Conference Presentations

- 4.1. C.I. Cano, E.S. Weiser and R.B. Pipes. "High Temperature Polymeric Microspheres and Foams: Liquid Phase Models." Presented at ANTEC 2003 (Annual Technical Conference of the Society of Plastics Engineers), Nashville, TN (May 2003).

  Abstract:

  The present paper focuses on the understanding of processes and property changes during formation of precursor forms of polyimides for high temperature foam applications. This understanding is to be used in the development of models for the void formation in the liquid state. The relationship of these voids to the initiation and formation of microspheres from the solid phase polymer particles will be discussed. Three sources of inflation pressure will be examined: organic compounds within the chemical structure of the polymer, volatiles released in the imidization process and residual solvents. The influence of reaction kinetics and molecular weight development on diffusion transport and viscosity within the polymer in both the liquid and solid phases will be examined to describe a major source of rate dependence of these phenomena.

Void topology within solid phase polymeric particles will be studied as a cause of the multiple microstructures realized in the foaming process.

- 4.2. C.I. Cano and R. B. Pipes. "Solid-State Polyimide Foaming From Powder Precursors: Effect of Particle Morphology on the Diffusive Phenomena." Presented at ANTEC 2004, Chicago, IL (May 2004).
  Selected for "Best of ANTEC 2004" Online Presentation Series of the Society of Plastics Engineers (Sept. 2004).
  (https://members.4spe.org/eLearning/courseDescription.cfm?cid=149).

  Abstract:
  Solid-state foaming of polyimide powder precursors is studied by examining concurrent and competitive phenomena that determine the morphology and physical properties of the foam unit cell. Effects of particle size and shape on bubble nucleation and growth will be addressed.

- 4.3. C.I. Cano and R.B. Pipes. "Polymeric Foams from Powder – Competitive Diffusion Prior to Bubble Growth." Presented at FOAMS 2004, 4th International Conference on Thermoplastic Foam Processing and Technology, Wilmington, DE (Oct 2004).

  Abstract:
  The present study examines the competition between elimination of the volatile species by diffusion and the inflation of polymeric bubbles in the powder foaming process from solid precursors. Solid poly(amic acid) (PAA) precursor is used for foaming into microspheres or foams depending on whether the powder particles are free or confined inside a volume. This precursor is produced in a prior process of size reduction where a solid-state solution is ground into smaller particles. It is this comminution process that imparts the precursor its major geometric features. The edges of these particles are sharp and angular; a common feature of brittle comminuted materials. Features such as voids and striations are present in the particles as well. These morphological characteristics influence the transport behavior of heat and mass through the particles during thermal treatment creating multiple scenarios for competitive diffusion.

5. Papers in Preparation:

There are 3 additional manuscripts which are in various stages of preparation. The anticipated titles and abstracts are provided below. Appropriate journals will be selected for submission.

- 5.1. "Modeling Particle Inflation from Poly(amic acid) Powdered Precursors I: Morphological Characteristics and Onset of Inflation"

  Abstract:
  Morphological characteristics of polyimide microstructures obtained by the solid-state powder foaming process impart the governing mechanical properties of the unit cell

to polyimide foams prepared from them. Morphological analysis of precursor particles has shown that particle size and shape, as well as the presence of embedded microvoids (nuclei) exert a strong influence on the final microstructure morphology. Of equal importance are processing conditions such as heating rate and primary blowing agent content in the particles prior to thermal treatment. In this paper, the first of two numerical schemes is presented. A numerical model has been developed and a parametric analysis has been performed on the governing parameters for particle inflation with the purpose of determining their effect on the onset of particle inflation and the potential morphological characteristics of polyimide microstructures. It has been found that precursor particle morphology and nuclei density are the key parameters in controlling the potential morphology of the microstructures by limiting the number of bubbles that grow within each particle. The second numerical scheme dealing with the bubble growth and cessation in precursor particles will be discussed in a later paper.

- 5.2. "Modeling Particle Inflation from Poly(amic acid) Powdered Precursors II: Morphological Development, Bubble Growth and Cessation of Growth".

Abstract:

The morphological development of polyimide microstructures from poly(amic acid) powders has been shown to depend highly on the morphological characteristics of the precursor particles as well as on the processing conditions at which they are treated through the inflation process. In the present paper, the second of two numerical schemes is presented. A numerical model for bubble growth has been developed to account for the effect of the different parameters in the final morphological development, as well as on the bubble growth kinematics and subsequent cessation of growth. This model is based on the first numerical scheme presented in an earlier publication where the conditions leading to bubble growth were analyzed. Several morphological characteristics on the precursor particles, as well as processing conditions have been shown to govern the kinematics of inflation and allow a clearer understanding of the solid-state foaming process.

- 5.3. "Polyimide Microstructures and Foams from Powdered Precursors: Phenomenology of Particle Inflation"

Abstract:

The present paper discusses the phenomenology of particle inflation from powdered precursors to produce polyimide microstructures and foams. These sphere-like microstructures are produced by the solid-state powder foaming process in which poly(amic acid) particles (of particle size 75 – 300 μm) with embedded blowing agents are subjected to thermal treatment thereby inducing internal bubble growth.

It has been observed that different physicochemical transformations take place during the inflation stages. Some of these transformations include amidation and imidization reactions, production of condensation volatile components that act as secondary blowing agents and blowing agent devolatilization among others. The study of physicochemical and morphological phenomena prior to and during the inflation process provides a comprehensive understanding for better process control and optimization.