Sol – Gel Modelling Associated with the Rheology of Polymeric Precursors of Ceramic Materials

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Abstract:
A general constitutive relation describing the change of viscoelastic behavior during the liquid - solid (sol - gel) transition which takes place in preceramic polymers is derived on the basis of Jeffrey's 3-constants model with time dependent viscosities and elasticity. It is postulated that the sol - gel - transition can be analyzed analogous to the solutions of the Avrami equation used for modeling crystallization processes. Two different polymer systems used as precursor for the production of ceramic materials are investigated here: i) a mixture based on polysiloxane, alumatrane and isopropanol; ii) a non-oxidic carbodiimide gel based on the reaction of chlorosilanes with bis(trimethylsilyl)carbodiimide. Continuous measurements of the dynamic moduli versus reaction time, as well as creep tests at constant shear stress, evidenced both qualitative similarities and quantitative differences associated with the sol - gel transition of the two polymer systems. The shear rate and viscosity dependence of reaction time in creep tests, respectively the evolution of Lissajous figures associated with oscillatory experiments, are found to be consistent with the numerical simulations of the proposed constitutive relation.

Zusammenfassung:
Eine allgemeine konstitutive Beziehung zur Beschreibung der Änderung des viskoelastischen Verhaltens während des flüssig-fest Sol-Gel-Übergangs präkeramischer Polymere wird auf der Basis des 3-Konstanten-Modells von Jeffrey unter Berücksichtigung der zeitabhängigen Viskosität und Elastizität abgeleitet. Lösungen der Avrami-Gleichung zur Modellierung von Kristallisationsprozessen werden hier zur Beschreibung des Sol-Gel-Prozesses herangezogen. Untersucht wurden zwei unterschiedliche Polymersysteme, die zur Herstellung keramischer Materialien verwendet werden: i) eine Mischung aus Polysiloxan, Alumatran and Isopropanol und ii) ein nicht-oxidisches Carbodiimid-Gel, hergestellt durch Reaktion von Chlorsilanen und Bis(trimethylsilyl)carbodiimid. Die hier untersuchten Phasenübergängen der beiden Sol-Gel Prozesse sind qualitativ ähnlich, zeigen jedoch quantitative Unterschiede wie kontinuierliche Messungen der dynamischen Moduli in Abhängigkeit der Zeit sowie Kriechtests bei konstanter Scherbeanspruchung ergeben haben. Die Abhängigkeit der Reaktionszeit von der Scherrate und der Viskosität in Kriechtests sowie das Auftreten von Lissajous Figuren in oszillatorischen Experimenten stehen im Einklang mit den numerischen Simulationen der hier vorgeschlagenen konstitutiven Beziehung.

Résumé:
Une relation constitutive générale qui présente le changement du comportement viscoélastique qui se produit pendant la transition liquide-solide (sol-gel) des polymères céramiques est décrite avec le modèle Jeffrey avec 3-constantes, modèle dans lequel la viscosité et l'élasticité dépendent du temps. On postule que la transition sol-gel peut-être analysée comme la solution donnée par les équations de Avrami, équations qui sont utilisées pour modeliser la cristallisation. Dans cet article sont analysés deux systèmes différents de polymères qui sont utilisés comme précurseurs pour la production des matériaux céramiques: i) une mixture de polysiloxane, alumatrane et isopropanol; ii) un gel non-oxidique carbodiimide basé sur une réaction du chlorosilanes avec bis(trimethysilyl) carbodiimide. Les mesures continuelles du module dynamique qui dépend du temps de réponse, mesures qui ont été réalisées avec des tests viscométriques à contraintes tangentielles constantes, mettent en évidence des similarités qualitatives et aussi des différences quantitatives qui sont associées avec la transition sol-gel pour les deux systèmes de polymères. La dépendance de la vitesse de cisaillement et de la viscosité en fonction du temps de réponse qui est relevée dans les tests viscométriques, et aussi l'évolution des figures de Lissajous associées avec les expériences oscillatoires sont en concordance avec les simulations numériques de la relation constitutive proposée.

Key words: constitutive relation, viscoelasticity, rheometry, Lissajous figures, sol - gel process, phase transition, ceramic precursors

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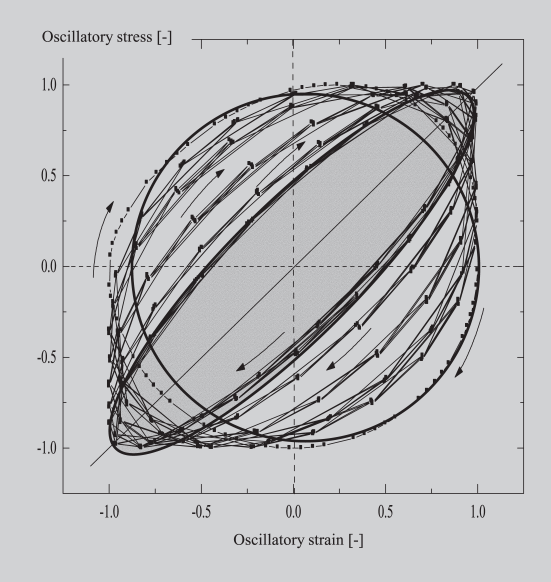

Figure 11: Experimental non-dimensional Lissajous figure for sample S2.

Structural characteristics and phenomenological properties define the sol - gel process. The correlation of the macroscopic changes during the liquid - solid transition with the evolution of chemical reaction is not completely understood and there is no comprehensive and complete model describing the change of viscoelastic properties. The main aim of our future research is to extend the rheological experimental investigations to the evolution of the normal stresses during gelation and to correlate the rheometry with a visualization technique of the growing network structure (Trappe et al. [23], Loren et al. [24]), and the evolution of diffusion coefficients (Romer et al. [25], Drabarek et al. [26]), respectively. We also intend to use other techniques like Small Angle X-ray Scattering to study structural changes in sol - gel transition and to correlate the results with the theoretical approach presented here, in order to gain a better understanding of liquid - solid transition in polymeric precursor in general, respectively to establish a correlation between the precursor properties and the structure of amorphous and crystalline ceramic, in particular.

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