Creep and Large-amplitude Oscillatory Shear Behavior of Whey Protein Isolate/κ-carrageenan Gels

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Abstract:
Dynamic oscillatory and creep tests are two common rheological methods used to determine viscoelastic properties. In the food industry, these tests are generally performed in the linear viscoelastic region, providing information on food structure and behavior over a range of timescales. However, this small-strain testing gives an incomplete picture of structural deformation and breakdown. Nonlinear oscillatory and creep testing, on the other hand, may yield a more complete fingerprint of food structural behavior. In this study, whey protein isolate (WPI)/κ-carrageenan gels with different structures were studied under large amplitude oscillatory shear (LAOS) and creep tests to determine the impact of structure on nonlinear oscillatory and creep behavior, and to examine correlations between nonlinear oscillatory and creep parameters. Evaluated structural types comprised a homogeneous protein gel, a bicontinuous gel, in which both WPI and κ-carrageenan exhibited a continuous network, and a carrageenan continuous gel. Creep data were fit to 4-element Burgers models for further analysis, and the predicted compliance values were found to be in agreement with experimental data ($R^2 \geq 0.90$). Carrageenan continuous gels showed the greatest degree of nonlinearity under LAOS (25 % strain), while homogeneous gels displayed the least. Nonlinear oscillatory data was found to correlate ($R^2 > 0.7$, $p < 0.05$) with parameters used in the 4-element Burgers model. Hence, nonlinear viscoelastic behavior among materials may be evaluated by both creep data and nonlinear oscillatory data. However, nonlinear oscillatory data gives a quantitative measure of the type and extent of nonlinear behavior, while creep data indicates only the presence of nonlinear behavior. By combining information on structural behavior derived from nonlinear oscillatory and creep data, it is possible to determine nonlinear behavior over a wide range of timescales, yielding insight into structural deformation and breakdown under application of stress or strain at different rates.

Zusammenfassung:
Dynamische oszillatorische und Kriechversuche sind zwei gängige rheologische Methoden, um die viskoelastischen Eigenschaften zu bestimmen. In der Lebensmittelindustrie werden diese Versuche i. Allg. im linear-viskoelastischen Bereich eingesetzt, um Informationen über die Struktur und das Verhalten der Lebensmittelsubstanz in einem bestimmten Bereich von Zeitskalen zu erhalten. Jedoch geben diese Tests bei geringen Deformationen ein unvollständiges Bild der strukturellen Deformation und des Aufbrechens. Nichtlineare oszillatorische und Kriechversuche dagegen können zu einem vollständigeren Bild des strukturellen Verhaltens der Lebensmittelsubstanz führen. In dieser Untersuchung wurden Molke-Proteinisolat (WPI)/κ-Carrageenan-Gele mit unterschiedlichen Strukturen untersucht bei Oszillationen mit großer Amplitude (LAOS) und Kriechversuchen, um den Einfluss der Struktur auf das nichtlineare oszillatorische Verhalten und die Kriecheigenschaften zu bestimmen. Ziel war, Korrelationen zwischen dem nichtlinearen Verhalten in Oszillation und in Kriechversuchen zu erhalten. Die untersuchten strukturellen Typen umfassten ein homogenes Proteingel, ein bicontinuierliches Gel, in dem sowohl WPI als auch κ-Carrageenan ein kontinuierliches Netzwerk aufwiesen, und ein kontinuierliches Carrageenan-Gel. Die Kriechdaten wurden mit einem vierelementigen Burger-Modell für die weitere Analyse angepasst. Die vorhergesagten Nachgiebigkeitswerte waren in guter Übereinstimmung mit den experimentellen Daten (R2 ffl 90). Die koninuierlichen Carrageenan-Gele wiesen den größten nichtlinearen Anteil bei LAOS auf (25% Deformation), während die homogenen Gele den niedrigsten Anteil aufwiesen. Die nichtlinearen oszillatorischen Daten korrelierten (R2 > 0.7, p < 0.05) mit den Parametern des vierelementigen Burger-Modells. Daher können das nichtlineare viskoelastische Verhalten zwischen den Materialien sowohl durch die Kriechdaten als auch durch nichtlineare oszillatorische Daten evaluiert werden. Jedoch geben die nichtlinearen oszillatorischen Daten ein quantitatives Maß des Typs und des Ausmaßes des nichtlinearen Verhaltens, während Kriechdaten nur auf die Existenz von nichtlinearem Verhalten hindeuten. Durch die Kombination der Information über das strukturelle Verhalten, die aus den nichtlinearen oszillatorischen und Kriechmessungen gewonnen wurde, ist es möglich, das nichtlineare Verhalten über einen großen Bereich an Zeitskalen zu bestimmen, um ein Verständnis der strukturellen Deformation und des Aufbrechens bei der Anwendung von Spannung und Deformation bei verschiedenen Deformationsgeschwindigkeiten zu erhalten.

Résumé:
Les tests de fluage et dynamique oscillatoire sont deux méthodes rhéologiques courantes utilisées pour déterminer les propriétés rhéologiques. Dans l'industrie alimentaire, ces tests sont généralement menés dans le régi-

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4 CONCLUSIONS

Gelation conditions of WPI/κ-carrageenan gels were varied to produce gels with three different microstructures: homogeneous (protein continuous), bicontinuous, and carrageenan continuous. Gel structure impacted the degree of nonlinear viscoelastic behavior as well as creep behavior. Regardless of gel structure, creep data was found to correlate to nonlinear viscoelastic behavior. Thus, evaluation of material nonlinear viscoelastic behavior is possible by creep testing as well as LAOS testing. Creep testing, however, only indicates the presence of nonlinear behavior, while nonlinear oscillatory testing yields a quantitative measure of the type and extent of nonlinear viscoelastic behavior. By combining information on structural behavior derived from nonlinear oscillatory data, such as strain hardening and softening, with viscoelastic behavior derived from creep data, nonlinear viscoelastic behavior may be determined over a wide range of timescales, yielding insight into structural deformation and breakdown under application of stress or strain at different rates. It is possible that nonlinear viscoelastic properties are related to other rheological properties, as well as textural properties and material breakdown patterns; however, further study is needed to determine the relationships between nonlinear viscoelastic properties and other large-strain rheological data, as well as sensory and oral processing data.

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