Extrusion Effects on the Mechanical Properties of Agar

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SYNOPSIS

The mechanical properties of extruded mixtures of Agar and water were measured for two formulations under slightly different extrusion conditions. The extrudate exhibits high tensile strength when moisture content is 30 wt % and very high elongation (> 2000%) when moisture content is 60 wt %. Electron micrographs of extruded samples at these extremes support the mechanical data. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Agar undergoes a thermoreversible sol-gel transformation,[1] although with considerable hysteresis. It gels at approximately 40°C or less, and melts at approximately 90°C upon heating. Thin, flexible, strong films can be made with very low concentrations of Agar (< 2%) using water as a solvent. The method of production can be a strong factor in governing the physical properties of the final product. For example, extrusion of synthetic polymeric films in general can orient molecules by shear, and different degrees of crystallinity can be incorporated into a product to achieve the desired properties. Similar behavior can be expected of Agar with respect to the degree of gelation and microstructure/property relations. Experimental results, some of which are reported herein, suggest that a wide range of mechanical and optical properties can be obtained under different conditions. For example, under some conditions, extruded Agar has high mechanical strength. Other processing conditions generate an extrudate with extremely high ultimate elongation (> 2000%).

Agar is a complex mixture of polysaccharides. The principle gelling agent is agarose, which has a disaccharide repeat unit consisting of a 3-linked-β-D-galactose residue connected to a 4-linked 3,6-anhydro-α-L-galactose residue.[2] Molecular weights are reported ranging from 3–9 × 10^3 to 10^6.[1-3] In addition, there are impurities and extra components in Agar that can affect the gelation mechanism. Agar lacks charged sulphate groups, and only very small amounts (0.1% w/w) are necessary to form a thermoreversible gel. With regard to crosslinking, it is possible that left-handed, double-helix formation is involved.[4] Junction zones are also postulated,[2,3,5] consisting of ordered chains separated by disordered regions along the chain contour. The disordered regions are generally shorter than random coil dimensions for network strands between crosslinks, as described by the theory of rubber elasticity. Gels normally contain very large amounts of water, suggesting that they are swollen. Obviously, no satisfactory treatment of these complex networks has been developed.[5] For example, the double-helix junction zone concept has been challenged with a single-helix model akin to synthetic polymer gelation.[2] Recent electron microscopic evidence[6] of neutralized Agar gels reveals interconnected long microfibrils that are 5–25 nm wide, whereas viscous solutions contain shorter microfibrils that are 1–2 nm wide. The structure of gels formed by cooling sols from above 90°C to ambient is similar to gels formed by neutralization. This indicates that long and/or wide microfibrils are required to form a gel. Earlier electron microscopy studies[7] focusing on the superstructure of beaded agarose indicated a fairly rigid polysaccharide matrix occupying a small percentage of the bead volume. The skeleton of beaded agarose is composed of thin filaments approximately 20 Å in diameter bundled in a side-by-side assembly. The pores or channels between filament bundles vary in shape and diameter up to 0.3 μm. Obviously, a complete picture of Agar's network structure is far from being established. Because gela-

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Table I Mechanical and Optical Properties of Extruded Mixtures of Agar and Water

Moisture %	Thickness mils	Fracture stress psi	% Strain @Failure	Optics	Flexibility
30	36	21,000	~ 12	opaque	brittle
60	20	5–6000	> 2000	clear	ductile

tion can occur in an extremely broad range of water concentrations and because extrusion is a widely used method for forming films and other shapes, we choose to focus on a range of water content that might bracket a practical set of conditions for film extrusion.

EXPERIMENTAL CONSIDERATIONS

Materials and Sample Preparation Methods

Food grade Agar (Meer Corp. NFS-100) was blended with tap water at ≈ 30% and 60% w/w water concentrations. The 30% mixture was extruded in a $\frac{3}{4}''$ Brabender extruder through a $\frac{1}{4}''$ wide slit die. The L/D ratio was 20 : 1, with a 1 : 1 screw compression ratio, and the temperature at the screw tip was 120°C. The thickness of the product was 36 mils, or 0.036 inches. A slotted barrel was employed. The 60% mixture was also extruded through a $\frac{3}{4}''$ Brabender but it had a 15 : 1 L/D ratio and a smooth barrel surface. A 2″ wide die was used, and the temperature at the screw tip was 100°C. The thickness of the sample product was 20 mils in this case. All extruded materials were allowed to dry at ambient conditions and were maintained at ambient temperature for further testing.

Mechanical Properties

Uniaxial tensile deformation properties and stress–strain hysteresis for the Agar/60% water extrudate were measured at ambient temperature using a servohydraulic INSTRON™ model 8501 stress–strain apparatus. The Agar/30% water extrudate was tested on an ATS 9000 machine. A strain rate of 0.01 inch/s was employed in both experiments. Analysis of the results was accomplished through computerized data acquisition systems. Test specimens conformed to ASTM (D 638M) dimensions. For the Agar/60% water extrudate, pneumatic grips from Lloyd Instruments

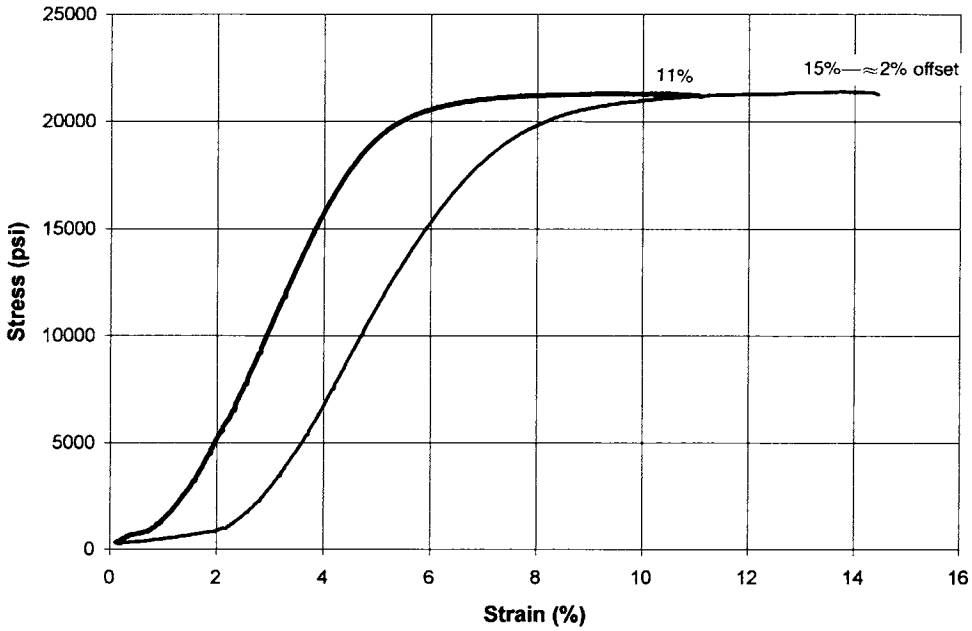

Figure 1 Stress–strain data for the 30 wt % material (two independent runs). Fracture occurred in both experiments.

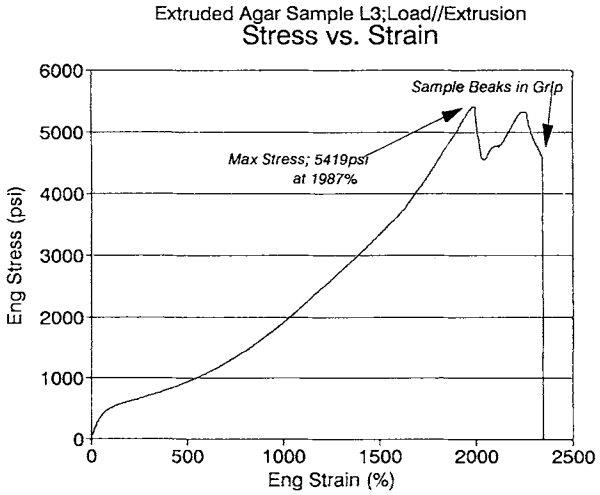

Figure 2 Stress–strain data from an Instron tensile test on the Agar/60 wt % water extrudate that exhibits more than 2000% elongation at failure.

were used to prevent sample slippage, although some slippage did occur at very high elongation ($\approx$ 1900% strain, as illustrated in Fig. 2).

Transmission Electron Microscopy

Lead-stained edge sections were observed and photographed in a JEOL 2000 Ex II transmission electron microscope.

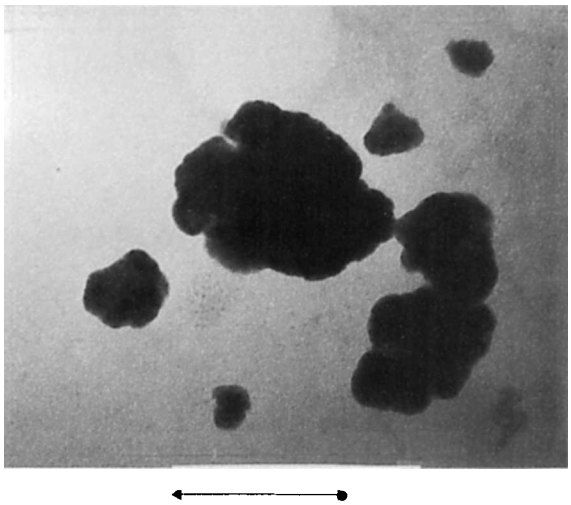

Figure 4 TEM micrograph of the Agar extrudate that was processed at low water content (i.e., 30 wt %).

RESULTS AND DISCUSSION

Mechanical Properties

The data in Table I summarizes the optical and ambient temperature mechanical properties of two formulations of Agar. The ultimate elongation of the Agar/60 wt % water extrudate at a draw rate of 0.01 in/s is remarkable in comparison with the strain at

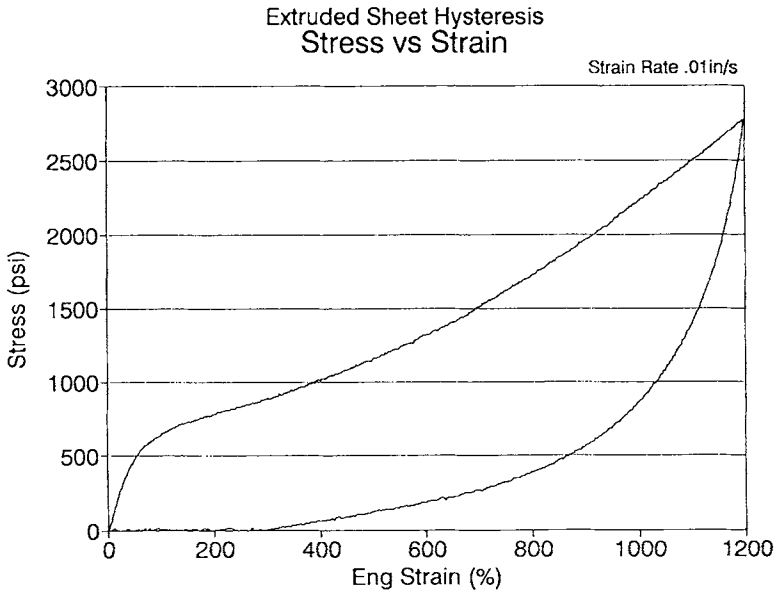

Figure 3 Stress–strain hysteresis response for the Agar/60 wt % water extrudate illustrating 1200% strain and irrecoverable deformation of 300% after one cycle.

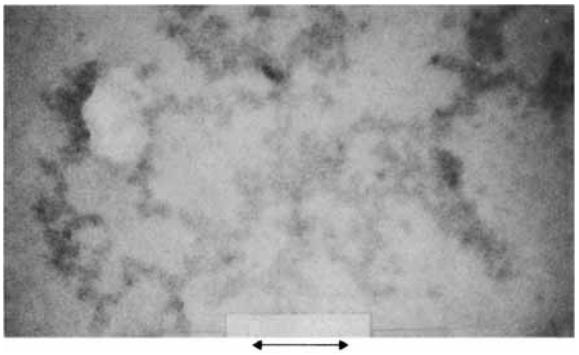

Figure 5 TEM micrograph of the Agar extrudate that was processed at high water content (i.e., 60 wt %).

failure for other macromolecules. Ultimate elongations on the order of 2000% exceed, by more than a factor of 2, expensive polyurethane thermoplastic elastomers,[8] for example. The lower moisture content sample exhibits a fracture stress approximately one-third that of steel (see Fig. 1).[9] The measured value reported herein is based on the initial cross-sectional area of the test specimen; the engineering fracture stress. Because most isotropic engineering materials exhibit lateral contraction under tension, as dictated by a Poisson ratio that is greater than zero, the 21,000 psi fracture stress entry in Table I represents an extreme lower limit of the true fracture stress for the lower moisture content sample. The higher moisture content sample has good tensile strength and extremely high elongation. Because the elongational properties of the higher moisture content material are so extraordinary, more detailed results on this material are presented in Figures 2 and 3. Again, note the unusual amount of elongation and the degree of hysteresis. When materials exhibit exceedingly large strains at failure, obvious questions arise that address potential energy dissipation mechanisms associated with the deformation process. Agar exhibits considerable stress–strain hysteresis at ambient temperature. When an extruded sheet was subjected to stress–strain cycling at a deformation rate of 0.01 inch/s, a permanent set of 300% strain was observed after one cycle that produced a maximum strain of 1200%. This phenomenon is illustrated in Figure 3.

For comparative purposes, there are no literature data on the mechanical properties of Agar at the relatively low water concentrations used in this study. Even at high water concentrations, McEvoy et al.[5] mention difficulties in obtaining stress–strain data for aqueous gels containing 1 wt % Agar, and don't present stress–strain curves that can be compared with our results. McEvoy et al. [5] did measure break strengths for ring shaped gels of 1–2 psi.

Transmission Electron Microscopy

Transmission electron micrographs (TEMs) of both lead-stained materials from Table I are illustrated in Figures 4 and 5. These micrographs are consistent with the mechanical properties reported in Table I. Shear within the extruder is able to break down the dry grains fed to the extruder for the lower moisture content material, but there may be insufficient water for swelling. Consequently, a dense structure develops, as illustrated in Figure 4, which results in high tensile strength and low elongation. The Agar–water mixture, which was extruded at higher moisture content, allows for the development of a swollen network of strong fibrils with a large amount of interfibrillar space, as illustrated in the micrograph of Figure 5. This rather low fibril density is responsible for an ultimate elongation that exceeds 2000%. It is also reasonable that these low-density fibrils dictate mechanical fracture in the vicinity of $\approx$ 6000 psi.

CONCLUSION

Much work needs to be done to elucidate the relationship between the microstructure and mechanical properties of Agar. Heretofore, to the best of our knowledge, the extensional properties of extruded Agar have not been measured. Because the properties uncovered in this work are most unusual, it is important that structure/properties relationships be further researched in order to foster the understanding of how processing affects properties. This understanding will open the door for new applications of this unusual macromolecule, which may be worthy of biomimicry.

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