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NEW FOODS FOR MILITARY USE. A PHYSICO-CHEMICAL APPROACH TO RESEARCH AND DEVELOPMENT.

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INTRODUCTION

Low and intermediate moisture foods have proved to be one of the most valuable of the various types of processed foods used in special combat feeding situations. The Long Range Patrol food packet, foods designed for space missions, and items used in the feeding of large groups of soldiers stationed in areas where resupply with fresh foods is difficult are examples of their usefulness. In view of their small volume and weight, their nutritional interchangeability, their long-term stability without refrigeration, and the fact that in most cases rehydration or other preparation is not necessary for consumption, these foods represent a new orientation in logistical flexibility and simplicity. One of the most complex problems that arises with such products is deterioration in texture. Brittleness, dryness, or excessive hardness are typical of the unwelcome textural changes that may occur. A related problem is the fragmentation and pulverization of leafy or fibrous dried foods which occur during storage and transportation. In existing rations, similar problems have caused substantial logistical and monetary losses to the Armed Forces. In the investigation here reported, a basic understanding of the relationships between the sorption of water and textural properties was sought. A thermodynamic approach to describing and interpreting the structural alterations that occur is set forth, and suggestions are made regarding how the findings can be utilized in tailoring the textural properties of dry foods to meet specific military needs.

THEORETICAL ANALYSIS

The adsorption of water vapor by the dry food results in both structural and physico-chemical changes. The structural changes can be measured by mechanical and sensory methods. The physico-chemical changes can be examined on the basis of the changes of the

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following thermodynamic functions: Enthalpy, $\overline{\Delta H}^{o}$, or heat content. Since the adsorption of water vapor by the food is an exothermic process, heat is released. This heat produces a mouth-drying sensation when the food is mixed with the saliva during chewing. Entropy, ΔS^{o}, or "degree of randomness". This is related to (a) the mobility changes of water molecules as they are adsorbed from the higher randomness (higher entropy) in the vapor to the lower randomness (lower entropy) on the food surface, and (b) the resultant structural alterations of the food, such as changes in crystallinity and swelling. Free energy, $\overline{\Delta F}^{o}$, which relates the enthalpy and entropy functions. This is a measure of the feasibility or "spontaneity" of a reaction. The above thermodynamic functions can be easily calculated on the basis of the moisture sorption isotherm (Figure 1). In the first part of this study numerical values of textural properties were obtained at different water activities of the isotherm, using three different instruments. The term "water activity", Aw, is equal to the ratio P/P_o, where P is the vapor pressure of water in the food and P_o the saturation vapor pressure of pure water at the same temperature. In the second part, the thermodynamic functions, calculated from the isotherm values, were used to gain an insight into the effects of Aw on mechanical characteristics.

MATERIALS AND METHODS

Samples from precooked, semimembranosus muscles of various beef animals were dehydrated to different residual moisture contents using a freeze-desiccation process developed by NLABS and reported here two years ago (7). The test specimens were circles of meat of 38 mm diameter and 12 mm thickness. In addition, commercially-processed, bite-size samples of dehydrated beef sandwich, chicken sandwich, cheese sandwich and chicken cubes were studied. Detailed accounts of the materials and methods have been published elsewhere (2). The mechanical texture properties of the food at different water activities were determined by three instruments, which involve testing by cutting, by compression or by penetration.

Cutting tests were performed using the Allo-Kramer Shear-Press. The use of this instrument involved cutting the sample between the multiple bars of a moving crosshead and the corresponding stationary cell surface. Results were expressed as maximum cutting force.

Compression tests were performed using the Instron Universal Testing Apparatus, equipped with a cylindrical, flat-surface punch of 57 mm diameter. The speed of the punch was 20 mm/min. The samples were compressed to 25% of initial thickness (loading), and they were subsequently "decompressed" to zero force (unloading). A second loading-unloading curve was then obtained. Using these curves, the following mechanical texture properties were calculated (4, 6): Secant modulus - ratio of stress (compressive force per unit area) to strain (ratio of the depth of compression to the initial sample thickness) at 3.5% compression. This is a measure of rigidity or stiffness. Degree of elasticity - the ratio of elastic deformation to the sum of elastic and plastic deformation. Toughness - the work per unit volume necessary to compress the sample to the point of rupture. Crushability index - the ratio of the non-recoverable to recoverable work, as computed from the first loading/unloading curve. Work ratio - the ratio of the area under the loading part of the second curve to the area under the loading part of the first curve. This has been used as a measure of "cohesiveness". All Instron measurements, except the secant modulus, (specified above), refer to 25% compression.

Penetration tests were performed using the Masticometer, developed at the Swedish Institute for Food Preservation Research to simulate the forces and motion of the human jaw during chewing (2, 3). For this purpose, a testing punch moves downward and upward in a sinusoidal pattern, penetrating the sample to different depths. From the recorded curves, the maximum force of penetration ("hardness") and other textural properties are calculated.

The physico-chemical measurements included the determination of moisture sorption isotherms at 7, 25, and 37°C using a modified McBain-Bakr sorption apparatus. On the basis of these isotherms, the following physico-chemical values were calculated: Brunauer-Emmett-Teller (B.E.T.) value for a monomolecular layer of water; standard differential heat change of sorption according to the Clausius-Clapeyron equation; and standard differential entropy and free energy changes (5).

RESULTS AND DISCUSSION

Our results show that relationships between mechanical properties of foods and thermodynamic values can be used to establish a scientific basis for improving the textural quality of dehydrated foods. Results of measurements of textural properties will now be presented and their relation to thermodynamic properties discussed.

Measurements of Textural Properties

Results of cutting tests (Allo-Kramer Shear-Press) of precooked, freeze-dried beef are shown in Figures 2-4. The following observations were made: (a) Increasing moisture content from 0 to 11% (Aw 0-0.55) caused an increase of the cutting force value in a non-linear manner (Figure 2), indicating an increase of the hardness of the food. (b) These same conditions caused an increase of the dispersion of force values. This indicates that increasing moisture causes a better differentiation of the inherent textural variability among samples from different positions of the muscle. The data were treated further in order to explore meaningful relationships. Of the methods employed (graphical and polynomial fittings), the plot of force versus $(\% H_2O)^2$ indicates straight line relationships. (Similar results were obtained with semilogarithmic plots; however, comparisons of goodness of fit by use of root mean square differences favored the force versus $(\% H_2O)^2$ plot). Regression lines from these data are shown in Figure 3. Although confidence limits about the regression line cannot be established due to the increasing dispersion of force values, the regression line is useful in predicting an average force value for precooked, freeze-dried beef, making use of only a limited number of experimental measurements. These findings, supplemented by other information, are of practical value in the establishment of objective requirements in procurement specifications. (c) A reversal in the force versus Aw relationship appeared at about Aw 0.85 (Figure 4). This reversal occurs within the Aw region of the "intermediate moisture foods". From a practical standpoint, this finding provides a means for tailoring the mechanical properties of these foods through the control of water activity.

Results of compression tests (Instron Universal Testing Apparatus) are shown in Figure 5. It is obvious that important changes of textural behavior of the food occur within about Aw 0.15 and 0.30. The secant modulus, which is a measure of rigidity, attains a sharp maximum at about Aw 0.18, and subsequently drops to a low value at about Aw 0.26. The work ratio, which is a measure of "cohesiveness" (2), attains a maximum at about Aw 0.18 and a minimum at about Aw 0.26. Opposite to this is the change of the crushability index or "brittleness", which shows a minimum at about Aw 0.18 and a maximum at about Aw 0.26. Well-defined changes within Aw 0.15-0.30 were also exhibited by the degree of elasticity and toughness (cf. Figure 8).

Results of penetration tests (Swedish Masticometer) of low moisture foods are shown in Figure 6. The appearance of maxima and minima in the different curves close to Aw 0.20 bear certain similarities to the results discussed above with regard to compression testing.

The above results of compression and penetration tests are of wide applicability with the class of "low moisture foods", in view of the high correlations between mechanical properties and consumer sensory ratings (3). Important attributes of quality and acceptability, such as fragility, elastic properties and toughness can be effectively modified, or "built into" the food through the control of Aw to meet specific military needs.

Relationships Between Texture and Thermodynamic Properties

Plots of moisture content (or corresponding water activity) versus standard differential thermodynamic changes of enthalpy, entropy and free energy are shown in Figure 7. The most important characteristics of these curves are the maxima which occur in the entropy $-\overline{\Delta S^{o}}$ and enthalpy $-\overline{\Delta H^{o}}$ functions. The first maximum appears at about n 0.25 (n = moles of water/100 g non-fat dry solids) or Aw 0.13. This is slightly below the B.E.T. monomolecular layer of n 0.28. The second maximum occurs at about n 0.38 or Aw 0.34. The entropy relationships are the more informative among the thermodynamic changes. The increase of the entropy $-\overline{\Delta S^{o}}$ values with increasing moisture as the B.E.T. monolayer value is approached is due: (a) to lateral interactions in the adsorbed film which are caused by the restrictive effect of adsorbed water molecules, as the available sorptive sites become saturated, and (b) to structural alterations of the food. It is this second part of the total entropy which is of interest with regard to mechanical measurements. Since in natural food systems differentiation of the two parts is not possible, the total entropy change serves as an indirect index of the structural changes involved. Work on simple biological materials suggests that the increase of the $-\overline{\Delta S^{o}}$ values toward the first maximum is due to increased crystallinity and to the formation of a tightly bound food matrix (4). As shown in Figure 8, these changes result in maximum rigidity (secant modulus), toughness, cohesiveness (work ratio) and degree of elasticity. Higher rigidity indicates that a greater force is necessary to produce a given amount of deformation. The deformed material maintains strong recovery characteristics, a fact which is commensurate with a high cohesiveness. The second maximum in the entropy and enthalpy curves indicates a swelling process, as new polymer surfaces become accessible to water through the breaking of polymer-polymer bonds (1, 4).

SUMMARY AND CONCLUSIONS

An objective means of tailoring the mechanical texture properties of a new class of low and intermediate moisture foods to meet specific military needs has been introduced by controlling the water activity, Aw. This investigation has shown that:

(1) It is possible to predict an average cutting force value between Aw 0-0.75, making use of only a small number of experimental measurements. A reversal of the curve of force *versus* Aw was observed at about Aw 0.85. This information is of particular interest in the improvement of existing and development of new intermediate moisture foods. It provides the guidelines for the establishment of objective requirements of textural quality.

(2) A number of textural properties, measured by compression or penetration testing, reach a maximum or minimum value in the Aw range of 0.15 to 0.30. This is important in the development of low moisture ration items, and in providing objective criteria for specification purposes.

(3) A thermodynamic analysis of the moisture sorption process, applied to natural foods for the first time, provides a research tool for gaining an insight into the alterations of structure, insight which, due to the complexity of the material, is virtually impossible to obtain by other means.

The above relationships provide a scientific basis for development of special foods in place of artful empiricism. The effects of processing, transportation, storage and composition variables on the mechanical characteristics of new foods can be rapidly assessed, and improved prototypes can be designed and tested.

REFERENCES

1. Bettelheim, F. A. and S. H. Ehrlich. 1963. Water vapor sorption of mucopolysaccharides. J. Phys. Chem. <u>67</u>, 1948.
2. Kapsalis, J. G. 1967. Hygroscopic equilibrium and texture of freeze-dried foods. Tech. Rpt. AD655488. Clearinghouse for Federal, Scientific & Technical Information, Springfield, Va.
3. Kapsalis, J. G., B. Drake, and Birgit Johansson. 1969. Textural properties of dehydrated foods. Relationships with the thermodynamics of water vapor sorption. J. Texture Studies <u>1</u>, 80.
4. Kapsalis, J. G., J. E. Walker, Jr., and M. Wolf. 1970. A physico-chemical approach to the study of the mechanical properties of low and intermediate moisture foods. J. Texture Studies <u>1</u>(2) (In press).
5. Lewis, G. N., and M. Randall. 1962. Thermodynamics, 2nd Ed., McGraw-Hill, New York, N. Y.
6. Mohsenin, N. N. 1968. Physical properties of plant and animal materials. Vol. I, Pennsylvania State University Press, University Park, Pa.
7. Strasser, J., J. G. Kapsalis and J. W. Giffee. 1968. Freeze desiccation - a new method of food preservation. Proc. Army Science Conference, Vol. II, 409, Westpoint, N. Y.

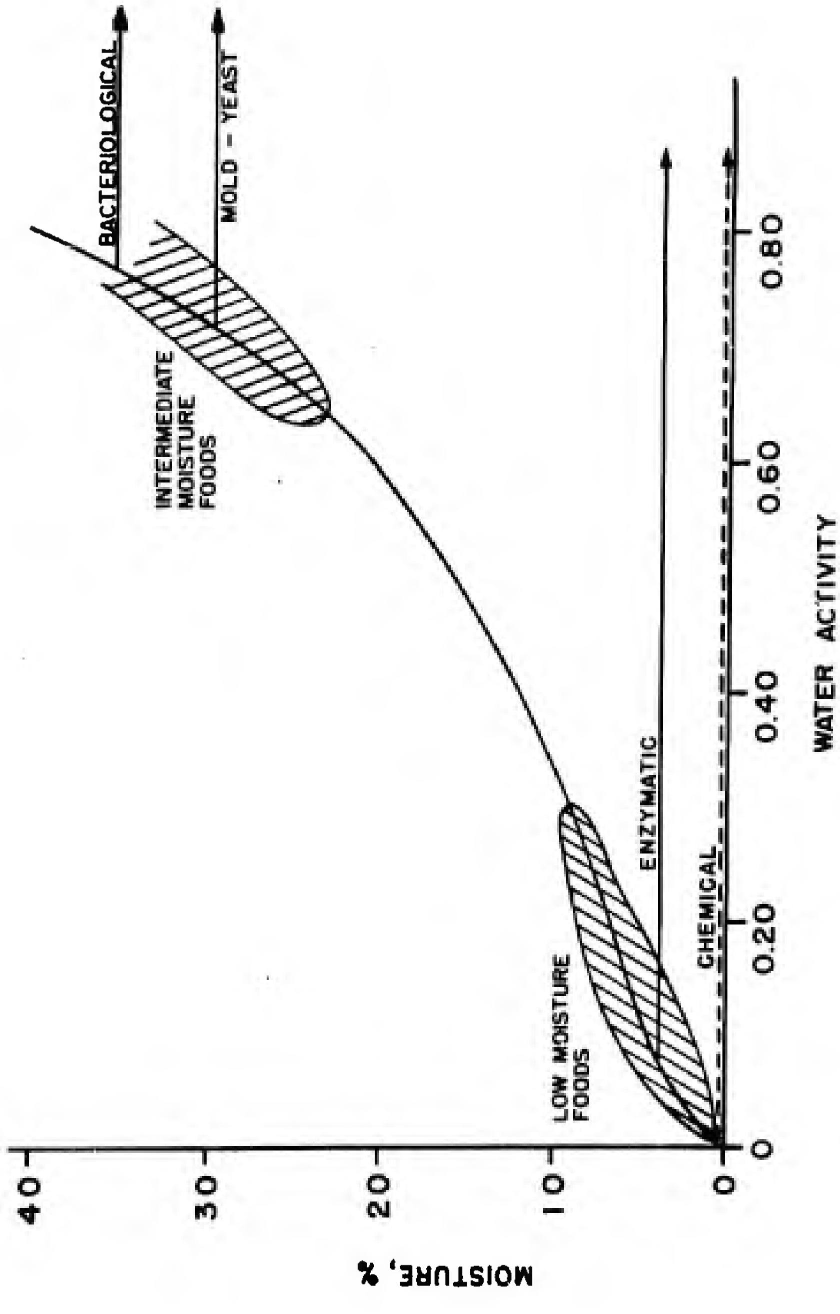

Fig. 1. Typical moisture sorption isotherm of a food product.

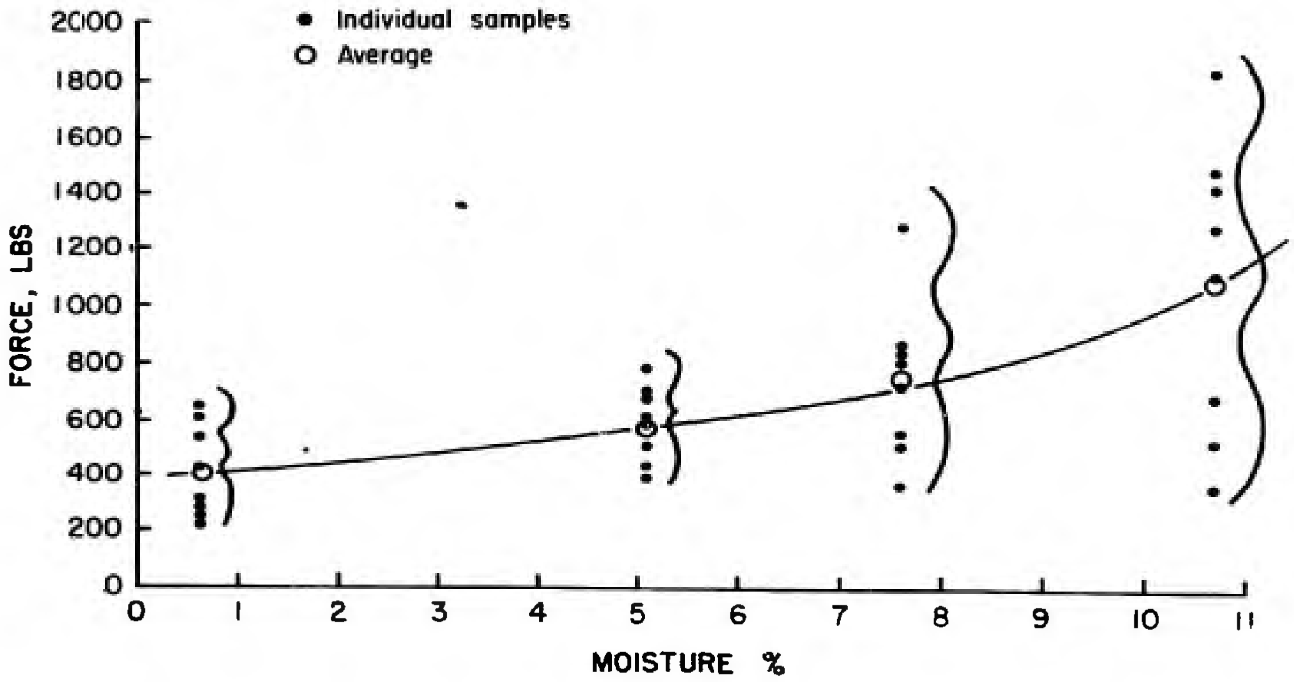

Fig. 2. Effect of residual moisture content on the cutting force value of precooked, freeze-desiccated beef. Cutting tests (Allo-Kramer Shear-Press).

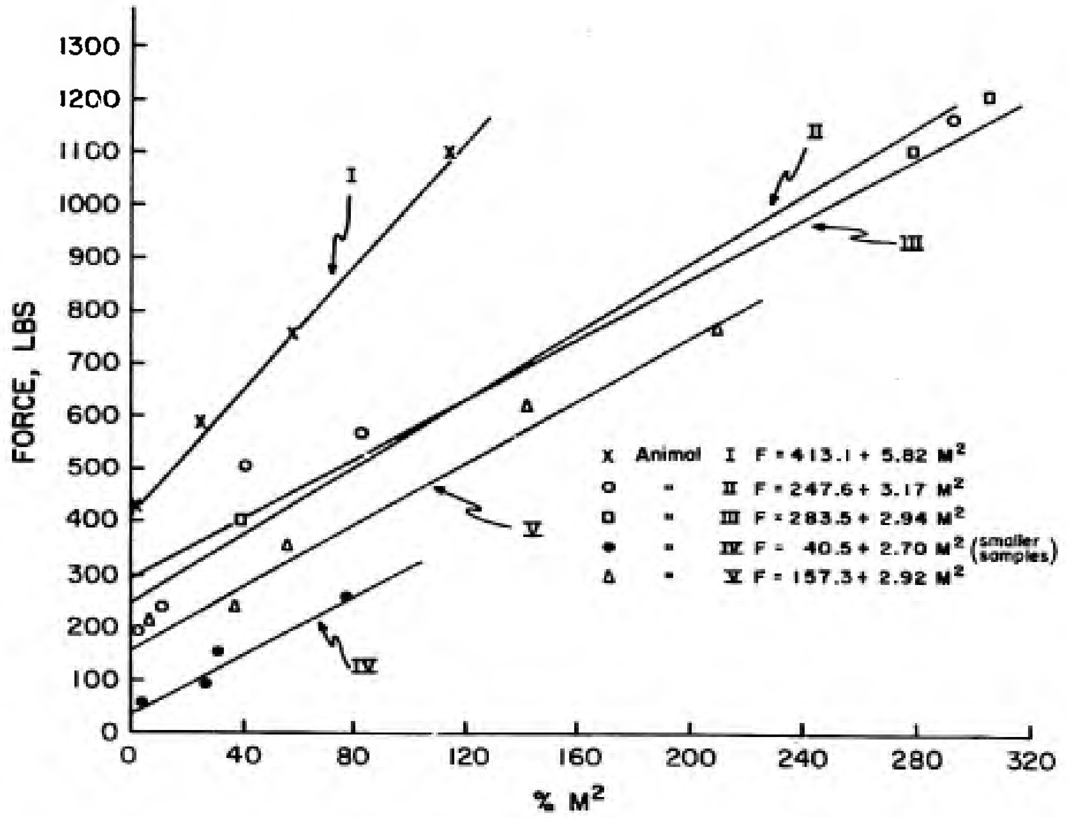

Fig. 3. Regression lines of cutting force vs. $(\%H_2O)^2$ in precooked, freeze-desiccated beef. Cutting tests (Allo-Kramer Shear-Press).

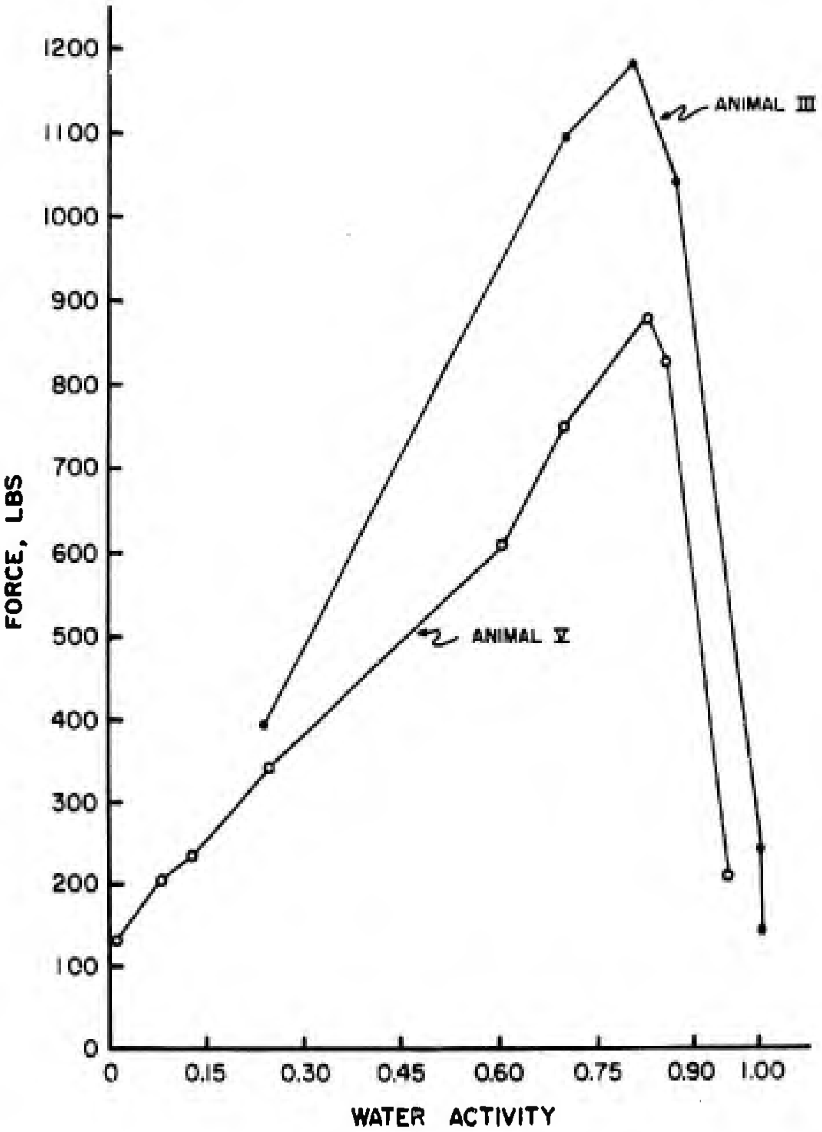

Fig. 4. Effect of water activity on the cutting force values of precooked, freeze-desiccated beef. Cutting tests (Allo-Kramer Shear-Press).

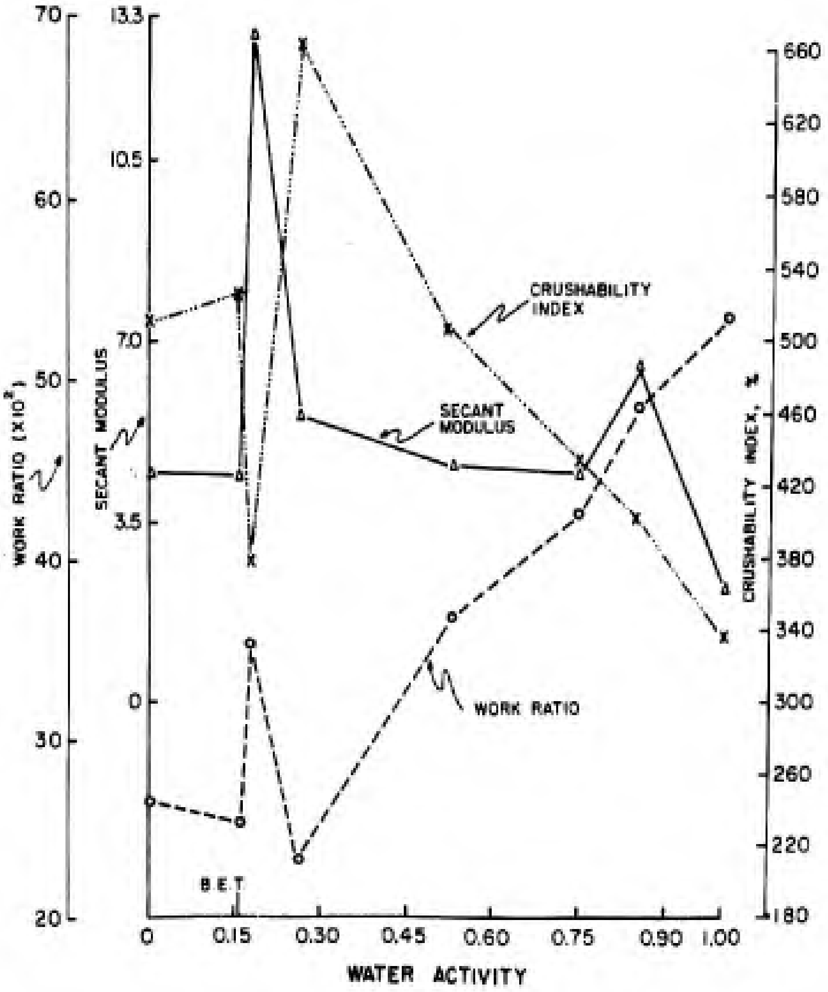

Fig. 5. Effect of water activity on textural properties of precooked, freeze-desiccated beef. Compression tests (Instron Universal Testing Apparatus).

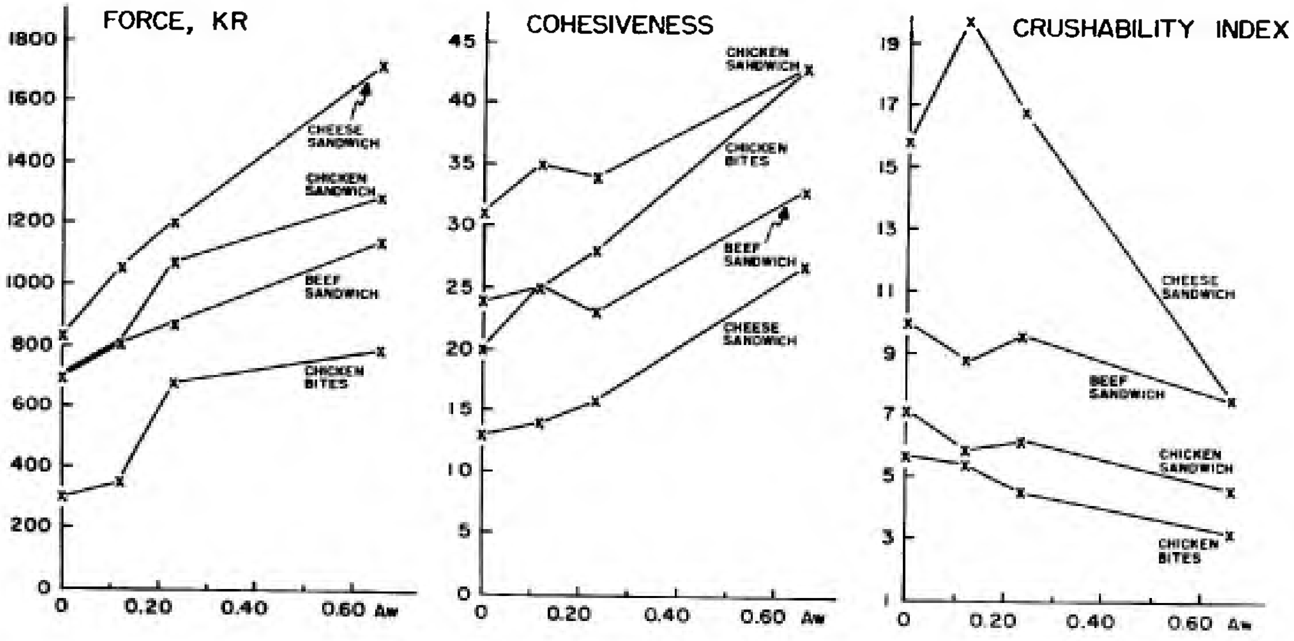

Fig. 6. Effect of water activity on the textural properties of bite-size special foods. Penetration tests (Swedish Masticometer). Force, KR = instrument relative units.

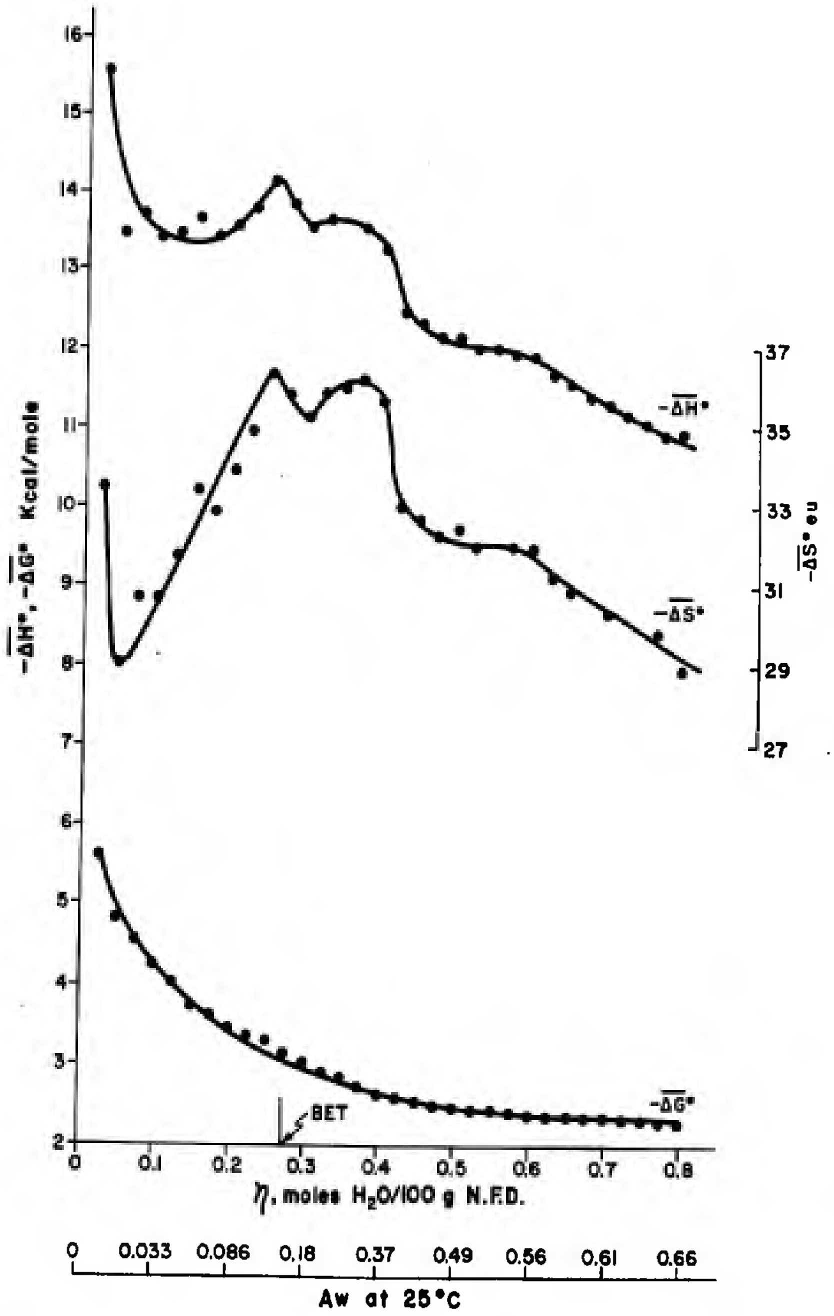

Fig. 7. Standard differential thermodynamic functions for adsorption of water vapor on precooked, freeze-desiccated beef. N.F.D. = non-fat dry solids.

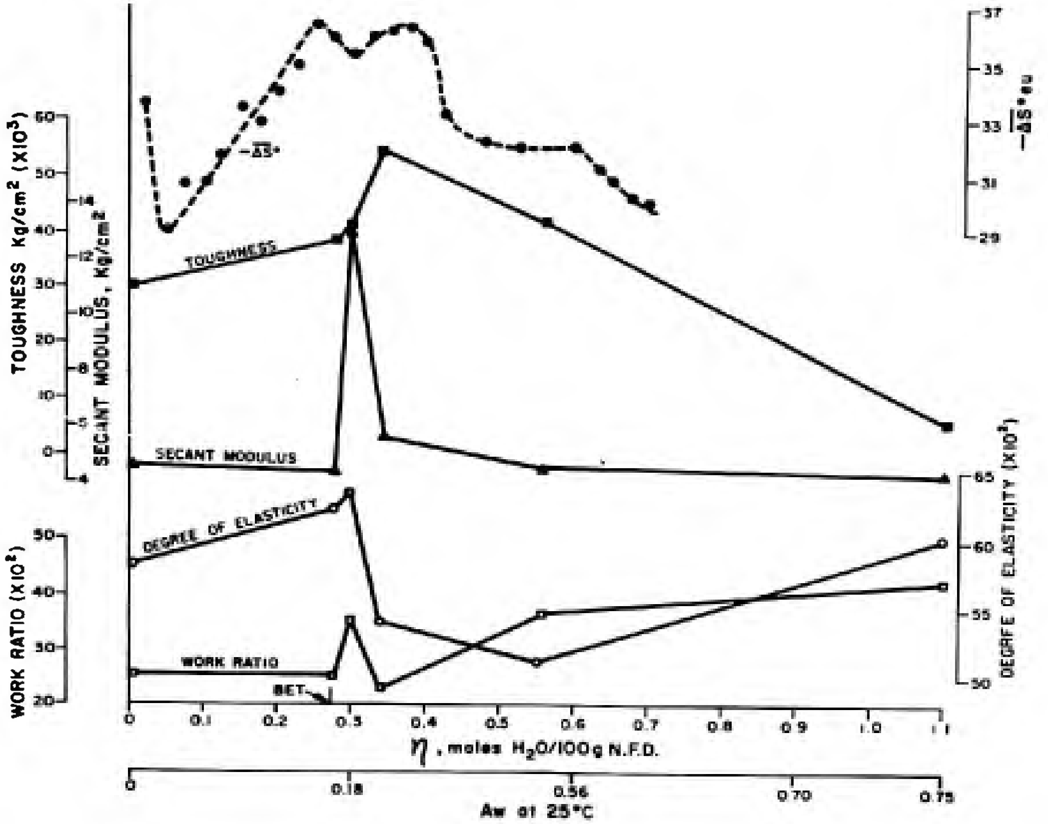

Fig. 8. Relationships between textural properties as revealed by compression testing and standard differential entropy change of water vapor sorption in precooked, freeze-desiccated beef. N.F.D. = non-fat dry solids.