

The Dahlquist Criterion: Applicability of a Rheological Criterion to the Loss of Pressure-Sensitive Tack in Flour-Water Dough¹

S. S. HEDDLESON,² D. D. HAMANN,² and D. R. LINEBACK³

ABSTRACT

Cereal Chem. 70(6):744-748

The relationship between the adhesive behavior (measured by probe tack) and dynamic rheological properties of a flour-water dough was examined over a selected temperature range. Flour-water dough probe tack was characterized in terms of the Dahlquist criterion for pressure-sensitive adhesives: tack ceased when the storage modulus was greater than 10^5 Pa. A maximum in the loss tangent (G''/G'), reflecting greater

viscous flow, corresponded with a maximum in tack energy. This was expected, since an adhesive must exhibit sufficient viscous flow when rate of deformation is low in order to conform to the adherend surface. These results suggest that the pressure-sensitive tack of flour-water dough to metal surfaces can be studied in terms of a rheological mechanism.

Adhesion plays a diverse functional role in many baked products. In some instances, it is desirable and necessary for appropriate baked product functionality, but often it interferes with processing. Scientists studying adhesive behavior quickly recognized that one mechanism could not explain all types of adhesion (Saunders et al 1992). Thus, adhesion scientists learned to specifically define the function of the adhesive first and then study adhesive behavior through the integration of a wide variety of specialized fields (e.g., rheology, structure-function relationships of polymers, and surface energetics).

In the case where application of a force to the surface of a wheat flour dough results in adhesion to processing equipment, a bond with some degree of cohesive strength is formed immediately with the equipment surface. This is analogous to the performance of pressure-sensitive adhesives (PSAs). PSAs, like wheat flour dough, are materials that are viscoelastic under conditions of use. The performance of a PSA depends on the viscoelastic response of the bulk material and on the surface energies of the adhesive and adherend (Chu 1989, Hammond 1989). When the surface energy of an adherend, e.g., metal, is much higher than that of the adhesive, e.g., an organic polymer, it can be assumed that the PSA performance is primarily governed by the viscoelastic properties of the adhesive material (Satas 1988, Hammond 1989).

An elastomer-resin system controls the viscoelastic properties of PSAs: the elastomer (rubbery polymer) provides an elastic component, and a low molecular weight tackifying resin constitutes the viscous component (Chu 1989, Schlademan 1989). This same type of system can also be found in the gluten component of wheat flour dough. Levine and Slade (1990) identified the elastomer portion of gluten as a high molecular weight glutenin and the resin portion as low molecular weight gliadins. This is reasonable, in light of the fact that, like PSAs, the low molecular weight gliadin (resin portion) has been described as the adhesive, viscous component, whereas high molecular weight glutenin (elastomeric portion) has been noted as being responsible for the non-adhesive, tough, elastic character of gluten (Ram and Nigam 1983, Bloksma and Bushuk 1988).

To function properly, the resin portion of PSAs must have a low molecular weight relative to the base elastomer (Wood 1987). Thus, a broad molecular weight distribution favors good tack and good cohesive strength (Casey 1989). Given this optimum broad molecular weight distribution, the storage modulus (G' , a dynamic measure of material elastic stiffness) at low frequencies (bonding time range) is depressed, improving wetting and bond

formation. Simultaneously, the high glass transition temperature of the low molecular weight resin raises the glass transition temperature of the elastomer-resin system. (Glass transition temperature can be determined by the maximum loss tangent, G''/G' ; it is the temperature above which amorphous polymers become soft and flexible [Murayama 1978]). This in turn elevates the storage moduli (i.e., higher forces are required to break the bond) at high frequencies (debonding time range) (Wood 1987, Chu 1989). Similarly, wheat flour-water doughs exhibit a low storage modulus in the time range for bonding (0.01 rad/sec) and a high storage modulus in the time range for debonding (100 rad/sec) (Navickis et al 1982, Dreese et al 1988). Like adhesion scientists, cereal scientists (Wrigley 1972) have suggested that molecular weight distribution is an important property governing the viscoelastic behavior of dough. The elastomeric portion of gluten generally has a broad molecular weight distribution (Kasarda et al 1971), thus making it naturally predisposed to having excellent PSA performance properties. Given the major role gluten plays in controlling wheat flour dough viscoelasticity (Janssen et al 1990), it follows that the multicomponent wheat flour dough would likely have excellent PSA performance properties as well.

Scientists studying the adhesion of dough to processing equipment have indirectly recognized the role of pressure-sensitive tack and cohesive strength. Andrianov et al (1968) demonstrated the influence of surface energy effects on the manner in which dough sticks to various probe materials. Rudolph and Tscheuschner (1979) and Dhaliwal et al (1990) recognized the influence of viscoelasticity on "stickiness" measurements and the cohesive strength of dough. Furthermore, food and adhesion scientists independently developed similar empirical testing methodology to characterize pressure-sensitive tack of their respective materials (Saunders et al 1992).

Carl A. Dahlquist, an adhesion scientist, discovered (Dahlquist 1959) that the complicated aspects of PSA tack values depend on molecular motions that determine viscoelastic relaxation times. He concluded that tack was a modulus-controlled process when the adhesive completely wet the adherend (complete wetting occurs when the adhesive surface energy is less than that of the adherend, as in the adherence of dough to a metal surface). He was the first to discover a rheological criterion for tack: tack did not occur when the adhesive storage modulus was greater than 10^5 Pa. This is known as the Dahlquist criterion and has since been confirmed (Kraus et al 1979, Foley and Chu 1986, Dale et al 1989, Han et al 1989) as applicable to a wide variety of elastomer-resin systems from which PSAs are formed. The Dahlquist criterion has thus formed the foundation for study of the rheological control mechanism of pressure-sensitive tack for PSAs. On the basis of this discovery, adhesion scientists have begun to utilize dynamic mechanical testing in conjunction with empirical testing to predict or evaluate how manipulation of PSA rheological behavior influences adhesive behavior.

Given the similarity of structure-function properties of PSAs and wheat flour dough, it was the objective of this study to

¹Paper FSR93-14 of the Journal Series of the North Carolina Agricultural Research Service, Raleigh.

²Graduate student and professor, respectively, Department of Food Science, North Carolina State University, Raleigh 27695-7624.

³Dean, College of Agriculture, University of Idaho, Moscow 83844-2331.

illustrate that the Dahlquist criterion is experimentally applicable to the pressure-sensitive tack behavior of wheat flour dough. Confirmation of the applicability of this rheological criterion suggests that further investigations of a viscoelastic mechanism responsible for controlling adhesion of dough to metal processing equipment would be useful.

MATERIALS AND METHODS

Flour

Wheat flour was supplied by Nabisco Brands, Inc. (Toledo, OH). The flour was a commercial blend of different cultivars having 8.6% protein, 0.44% ash, and 13.2% moisture (AACC 1983).

Test Sample Preparation

Doughs were mixed in a 300-g mixing bowl of a Brabender Plasti-Corder (model PL-MV101, C. W. Brabender Instruments, Inc., South Hackensack, NJ) at 30°C. Total moisture content of the dough was 40.8%. Mixing time was 2 min. Given the difficulty of machining "sticky" doughs, samples for adhesion and rheological testing were formed with a slit extruder nozzle at the same temperature and relative humidity conditions utilized during mixing. An environmental chamber (model RTT/1122S, Standard Environmental Systems, Inc., Totowa, NJ), designed to be used with a Universal Testing Machine (model 1122, Instron Corp., Canton, MA), was used to control temperature and relative humidity conditions during extrusion. The extruder consisted of a cylinder-piston arrangement (Kawanari et al 1981) supported by an aluminum stand. The brass cylinder had an inside diameter of 38 mm. The working length of the extruder cylinder was 220 mm. Extruder nozzle slit dimensions were 45 × 1.25 × 45 mm (length, width, and height, respectively). The brass extruder plunger was screwed onto the threaded end of an aluminum shaft, which was in turn driven by the Instron machine crosshead. A stainless-steel collar was secured around the top of the aluminum shaft. The shaft was screwed into the crosshead-mounted load cell until the collar contacted the load cell housing. The collar transmitted the extrusion force to the housing instead of to the sensing mechanism of the load cell. This prevented extrusion forces from exceeding the capacity of the sensing mechanism of the load cell, allowing use of the load cell for both extrusion (collar intact) and adhesion testing (collar removed).

Immediately after mixing, dough was placed into the extruder under constant temperature and humidity conditions (30°C, 65% rh). After a 10-min rest time, dough was extruded at a piston rate of 50 mm/min. The first portion of the extrudate strip was discarded. Extrudate required for adhesion testing was allowed to collect on a stainless steel plate, supported by the aluminum stand underneath the extruder. As the extrudate emerged, the stainless steel plate was moved horizontally by hand via an environmental chamber access port. Final sample length and thickness were 200 mm and 1.6 mm, respectively. The sample was covered immediately by six rectangular (80 × 25 mm) strips of polyethylene (1 mil) to prevent surface drying (relative humidity was difficult to reattain after the chamber door had been opened) during the time required to equilibrate the test sample to the required test temperature. (An appropriate constant-equilibration time [30 min] was predetermined by conducting time-temperature profiles in the test samples at the various test temperatures utilized.) One gram of the extruded sample was utilized for rheological testing. Sample preparation was completed under constant conditions for mixing and extrusion. Test temperature was altered only after the sample preparation had been completed.

Adhesion Measurements

After sample preparation was complete, the cylinder-piston extruder was removed from the environmental chamber; test temperature and relative humidity were set; and a probe tack test apparatus (Fig. 1), similar to that designed by Wetzel (1957), was screwed onto the aluminum shaft. The collar at the load cell end of the aluminum shaft was removed, activating the load

cell sensing mechanism. Test conditions were as follows: copper probe with a 20-mm diameter and a 0.8- μ m surface finish, 50-mm/min deformation rate, 5-sec contact time, 99.69-g contact force (3,111-Pa contact stress), 500-mm/min withdrawal rate. Keeping the latter conditions constant, the following dough temperatures were used to vary pressure-sensitive tack behavior in the dough: 21, 29.3, 37.6, 45.9, 54.2, 62.5, and 70.8°C.

A computer program in BASIC was developed to automate the test procedure and calculate probe tack and tack energy. Before conducting a probe tack test, the program required the following inputs: test material, contact time, contact rate, full-scale force, withdrawal rate, probe type, contact force, test temperature, and relative humidity. After these were entered and the sample was allowed to equilibrate to the test temperature over a 30-min period after extrusion, the probe was lowered until it was as close to the sample as possible, but not touching. The stainless-steel plate was pulled toward the operator, and the polyethylene strip that prevented surface drying was quickly peeled off. The sample was positioned underneath the probe, and the test was started via the computer. After starting the test, the computer signaled the Universal Testing Machine to lower the probe at a given deformation rate until all of the probe weight was on the sample. The probe was allowed to remain on the sample for a given time, generating the bonding portion of the curve (Fig. 2). The computer then signaled the Universal Testing Machine to raise the probe from the sample at a given withdrawal rate, generating the debonding portion of the curve (Fig. 2). Two measurements were recorded by the computer: probe tack (g), the maximum force of the debonding curve, and tack energy (μ J), the area under the debonding curve. Six repetitions were done per two independently mixed dough samples due to the highly variable nature of this empirical test.

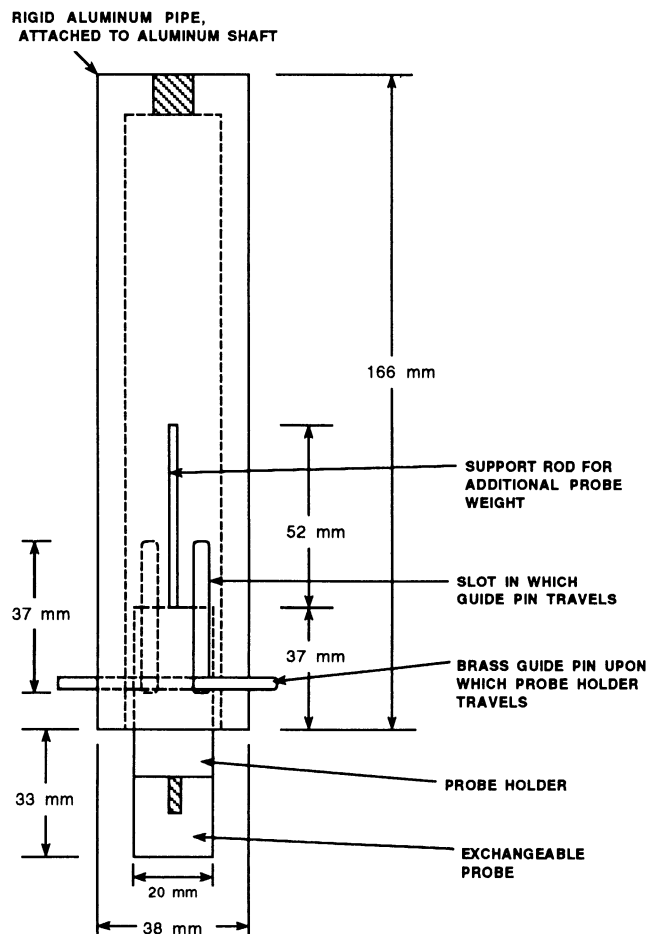


Fig. 1. Modified Wetzel probe apparatus consisting of a free-sliding probe holder to which a probe is attached. (Reprinted with permission. Satas 1989).

Rheological Measurements

Testing of the viscoelastic properties of the flour-water dough was done with a controlled strain rheometer system (model VOR, Bohlin Reologi, Lund, Sweden). This instrument measured the viscoelastic behavior of the dough over a given range of temperature at a constant frequency (1 Hz, approximately equivalent to the probe tack test bonding time). The test geometry consisted of a cone-and-plate system with a cone angle of 5.4° , and a 30-mm diameter. Test conditions were as follows: oscillation mode, 0.002 controlled strain, and a 41.349 g-cm torque bar. Dough temperatures tested were equivalent to those used in the probe tack test. Doughs were equilibrated 15 min after loading to permit the stress attained during sample compression to decay. A 10-min equilibration time between test temperatures was used to ensure that proper sample temperature was achieved. The elastic modulus (G') and the loss tangent (G''/G') were used to characterize the viscoelastic behavior of the dough. Measurements were repeated twice on two independently mixed dough samples immediately after extrusion due to the low variation associated with this fundamental test.

Manipulation of Dough Mechanical Behavior

To test the applicability of the Dahlquist criterion to wheat flour dough, the storage modulus of the dough must be raised to 10^5 Pa. Molecular motions influence material viscoelastic properties (Ferry 1980). Thus, four general experimental factors can be utilized to give equivalent changes in molecular mobility (Levine and Slade 1990): temperature, time, pressure, and concentration. Time-temperature equivalency procedures have been applied to dough systems with apparent success (Smith et al 1970), and Hibberd (1970) established an equivalency between time and concentration (water content) in dough systems.

Reaching the Dahlquist criterion requires a considerable decrease in molecular mobility; thus, the dough becomes extremely stiff at this level of storage modulus. There are equivalent methods of attaining this degree of dough stiffness. For example, water content (concentration) of the dough can be decreased to 35% (Navickis et al 1982). Unfortunately, the small motor on the Plasti-Corder could not provide enough power to mix a dough at this level of stiffness. Pressure can be decreased, but not with a constant strain rheometer. Strain rate (inverse time) can be greatly increased, but the data collection speed of the Instron was insufficient at these fast rates. Fortunately, the remaining variable, temperature, could be used because it avoided these equipment limitations. The observations of Dreese et al (1988) indicated that temperature (approximately 55°C) would effectively elevate the storage modulus, due to a change in dough structure resulting from starch gelatinization, to the Dahlquist criterion. The use of temperature to manipulate molecular mobility has also been favored by previous adhesion scientists investigating the existence of the Dahlquist criterion (Kraus et al 1979, Foley and Chu 1986, Dale et al 1989, Han et al 1989).

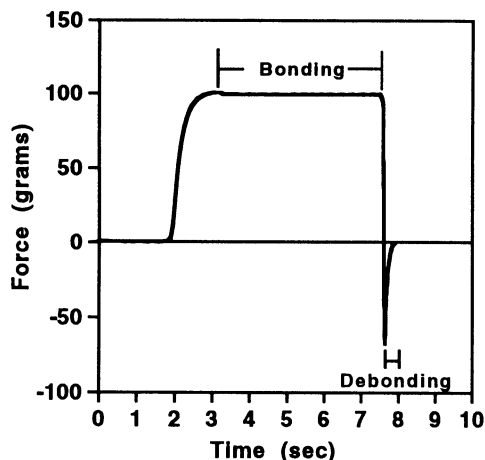


Fig. 2. Force-time curve generated during the probe tack test.

RESULTS AND DISCUSSION

Probe tack and tack energy variation with dough temperature are shown in Figures 3 and 4. Both measurements of tack increased with increasing temperature up to approximately $45\text{--}50^\circ\text{C}$, where they decreased dramatically. The coefficient of variation for the probe tack test was between 7 and 35%, a range not uncommon to tests measuring the ultimate (failure) properties of foods. Use of polyethylene strips to maintain the original dough surface long after extrusion was critical to successful probe tack testing. Removal of the strips created a minimal surface disturbance due to their low surface energy (adhesion of low-energy surfaces is not thermodynamically favorable) and the fast peel rate used upon removal (fast peel rate minimizes tack). A comparison of Figures 3 and 4 indicates that the probe tack curve did not show a sharp maximum value, as the tack energy curve did. Although cereal scientists usually favor the measure of the maximum force during debonding (probe tack), adhesion scientists have found tack energy to be a more meaningful parameter (Bates 1976). Comparing the changes in probe tack and tack energy with the storage modulus curve (Figs. 3 and 4), the tack energy is observed to better match the viscoelastic data. Probe tack and tack energy differ because tack energy values indicate whether cohesive or adhesive failure occurs. All samples in this study exhibiting tack failed cohesively, i.e., legging occurs during separation and residue is left on the probe after separation from the dough sample. When

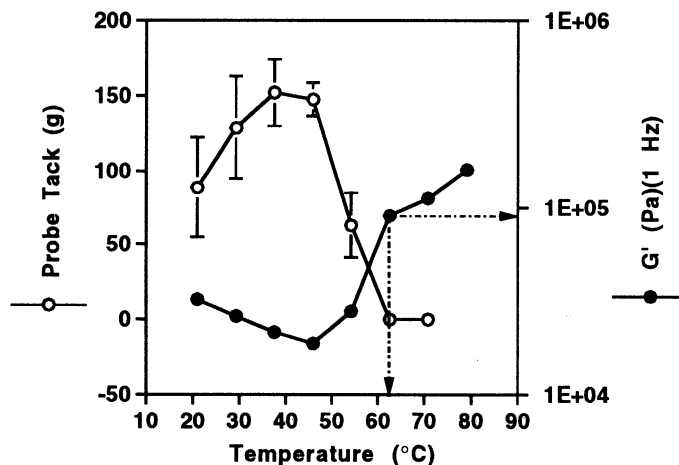


Fig. 3. Variation of probe tack and storage modulus (G') with dough temperature. The dotted line indicates that dough probe tack ceases when the shear storage modulus reaches approximately 10^5 Pa (the Dahlquist criterion).

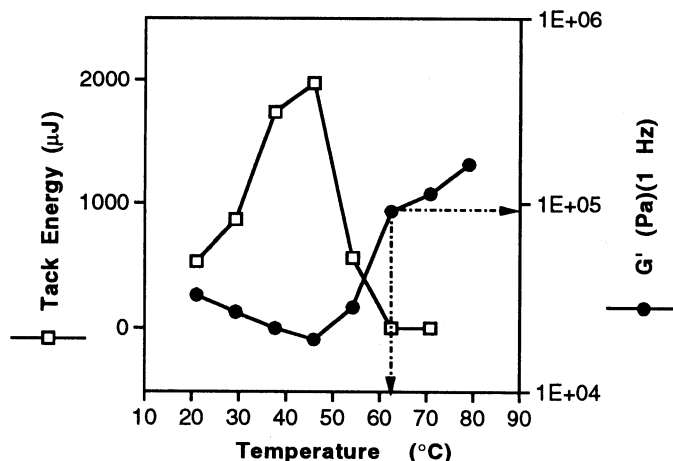


Fig. 4. Variation of probe tack energy and storage modulus (G') with dough temperature. The dotted line indicates that dough probe tack ceases when the shear storage modulus reaches approximately 10^5 Pa (the Dahlquist criterion).

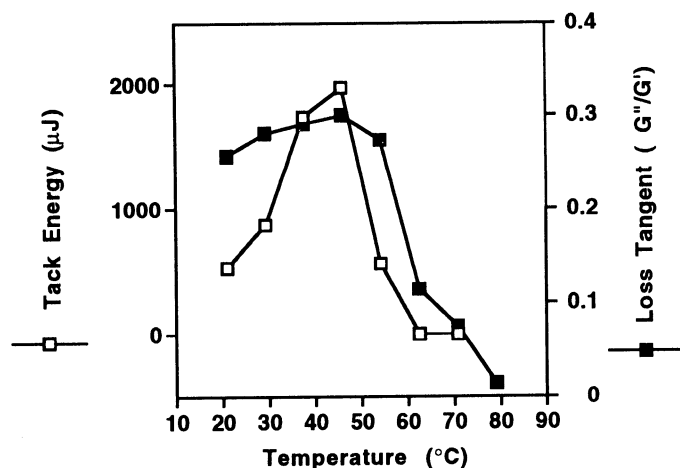


Fig. 5. Relationship between loss tangent and tack energy as they vary with temperature.

cohesive failure occurs, the debonding portion of the curve has a much greater area than when adhesive failure occurs.

Figure 3 indicates the relationship between dough probe tack and the storage modulus. Compared to the high-strain, empirical test of probe tack, the coefficient of variation for the fundamental, low-strain dynamic testing was much better, being only 3%. From 20°C to slightly less than 50°C, probe tack increased as the storage modulus decreased. After 50°C, the storage modulus increased and probe tack decreased. When the storage modulus reached the Dahlquist criterion, 10^5 Pa, tack ceased completely. Thus, loss of dough pressure-sensitive tack can be characterized in terms of the Dahlquist criterion typically used with PSAs.

Lindahl and Eliasson (1992) observed that an increase in phase angle (the angle whose tangent is the loss tangent, G''/G') was indicative of a "stickier" flour-water dough (as judged by a qualitative comparison of dough handling properties). This observation is not surprising, given that during bonding of a PSA, an adhesive must exhibit sufficient viscous flow, when rate of deformation is low, in order to conform to the adherend surface (Wood 1987). Their observation was confirmed by the quantitative data collected in this study (Fig. 5). Greater viscous flow is reflected by a maximum in loss tangent, which corresponds with a maximum in tack energy at 48°C. Above 48°C, loss tangent decreases rapidly (viscous flow decreases greatly), and a parallel decrease in tack energy occurs.

CONCLUSIONS

Using a concurrent approach of empirical (probe tack) and fundamental (dynamic mechanical testing) rheological measurement techniques, this study illustrated that the rheological criterion developed for the loss of pressure-sensitive tack in PSAs is applicable to the pressure-sensitive tack behavior of flour-water dough. This observation is the first step in developing and characterizing a viscoelastic mechanism(s) responsible for the control of wheat flour dough pressure-sensitive tack to metal surfaces.

ACKNOWLEDGMENTS

We thank Randolph Koch for his assistance in developing the probe tack computer program and Nabisco Brands, Inc., for their financial support.

LITERATURE CITED

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1983. Approved Methods of the AACC, 8th ed. Method 8-01, approved April 1961, revised October 1976 and October 1981; Method 44-15A, approved October 1975, revised October 1981; Method 46-12, approved October 1976, revised November 1983 and October 1986. The Association: St. Paul, MN.

ANDRIANOV, V. A., SHCHERBATENKO, V. V. and MIKULIN-

- SKAYA, L. R. 1968. Measurements of the adhesive strength of wheat dough to test materials. *Khlebopek. Konditer. Promst.* 12:5.
- BATES, R. 1976. Studies in the nature of adhesive tack. *J. Appl. Polym. Sci.* 20:2941.
- BLOKSMA, A. H., and BUSHUK, W. 1988. Rheology and chemistry of dough. Page 131 in: *Wheat: Chemistry and Technology*, 3rd ed. Vol. 2. Y. Pomeranz, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.
- CASEY, A. Z. 1989. Resin dispersions. Pages 545-566 in: *Handbook of Pressure Sensitive Adhesive Technology*. D. Satas, ed. Van Nostrand Reinhold: New York.
- CHU, S. G. 1989. Viscoelastic properties of pressure sensitive adhesives. Pages 158-203 in: *Handbook of Pressure Sensitive Adhesive Technology*. D. Satas, ed. Van Nostrand Reinhold: New York.
- DAHLQUIST, C. A. 1959. An investigation into the nature of tack. *Adhes. Age* 2:25.
- DALE, W. C., PASTER, M. D., and HAYNES, J. K. 1989. Mechanical properties of acrylic pressure sensitive adhesives and their relationships to industry standard testing. *J. Adhes.* 31:1.
- DHALIWAL, A. S., MARES, D. J., and MARSHALL, D. R. 1990. Measurement of dough surface stickiness with the 1B/1R chromosome translocation in bread wheats. *J. Cereal Sci.* 12:165.
- DREESE, P. C., FAUBION, J. M., and HOSENEY, R. C. 1988. Dynamic rheological properties of flour, gluten, and gluten-starch doughs. I. Temperature-dependent changes during heating. *Cereal Chem.* 65:348.
- FERRY, J. D. 1980. *Viscoelastic properties of polymers*. John Wiley & Sons: New York.
- FOLEY, K. F., and CHU, S. G. 1986. Rheological characterization of elastomer latexes for PSAs. *Adhes. Age* 29:24.
- HAMMOND, F. H. 1989. Tack. Pages 38-60 in: *Handbook of Pressure Sensitive Adhesive Technology*. D. Satas, ed. Van Nostrand Reinhold: New York.
- HAN, C. D., KIM, J., and BAEK, D. M. 1989. Viscoelastic behavior, thermodynamic compatibility, and phase equilibria in block copolymer-based pressure sensitive adhesives. *J. Adhes.* 28:201.
- HIBBERD, G. 1970. Dynamic viscoelastic behaviour of wheat flour doughs. II. Effects of water content in the linear region. *Rheol. Acta* 9:497.
- JANSSEN, A. M., VEREIJKEN, J. M., BEINTEMA, J. J., and WITHOLT, B. 1990. Rheological studies on gluten. Pages 180-186. in: *Gluten Proteins 1990*. W. Bushuk and R. Tkachuk, eds. Am. Assoc. Cereal Chem.: St. Paul, MN.
- KASARDA, D. D., NIMMO, C. C., and KOHLER, G. O. 1971. Proteins and the amino acid composition of wheat fractions. Pages 227-299 in: *Wheat: Chemistry and Technology*, 2nd ed. Y. Pomeranz, ed. Am. Assoc. Cereal Chem.: St. Paul, MN.
- KAWANARI, M., HAMANN, D. D., SWARTZEL, K. R., and HANSEN, A. P. 1981. Rheological and texture studies of butter. *J. Texture Stud.* 12:483.
- KRAUS, G., ROLLMANN, K. W., and GRAY, S. G. 1979. Tack and viscoelasticity of block copolymer based adhesive. *J. Adhes.* 10:221.
- LEVINE, H., and SLADE, L. 1990. Influences of the glassy and rubbery state on the thermal, mechanical, and structural properties of doughs and baked products. Pages 157-330 in: *Dough Rheology and Baked Product Texture*. H. Faridi and J. Faubion, eds. Van Nostrand Reinhold: New York.
- LINDAHL, L., and ELIASSON, A.-C. 1992. A comparison of some rheological properties of durum and wheat flour doughs. *Cereal Chem.* 69:30.
- MURAYAMA, T. 1978. *Material science monographs*. Vol. 1, Dynamic mechanical analysis of polymeric material. Van Nostrand Reinhold: New York.
- NAVICKIS, L. L., ANDERSON, R. A., BAGLEY, E. B., and JASBERG, B. K. 1982. Viscoelastic properties of wheat flour doughs: Variation of dynamic moduli with water and protein content. *J. Texture Stud.* 13:249.
- RAM, B. P., and NIGAM, S. N. 1983. Texturometer as a tool for studying varietal differences in wheat flour doughs and gluten proteins. *J. Texture Stud.* 14:245.
- RUDOLPH, H., and TSCHEUSCHNER, H. D. 1979. Adhesiveness in wheat doughs. *Baecker Konditor* 27:229.
- SATAS, D. 1988. Rheological properties and performance of PSAs. *Adhes. Age* 31:28.
- SATAS, D. 1989. *Handbook of Pressure Sensitive Adhesive Technology*. Van Nostrand Reinhold: New York.
- SAUNDERS, S. R., HAMANN, D. D., and LINEBACK, D. R. 1992. A systems approach to food material adhesion. *Lebensm. Wiss. Technol.* 25:309.
- SCHLADEMAN, J. A. 1989. Tackifier resins. Ch. 20 in: *Handbook of Pressure Sensitive Adhesive Technology*. Satas, D., ed. Van Nostrand Reinhold: New York.

- SMITH, J. R., SMITH, T. L. and TSCHOEGL, N. W. 1970. Rheological properties of wheat flour doughs, III. Dynamic shear modulus and its dependence on amplitude, frequency, and dough composition. *Rheol. Acta* 9:239.
- WETZEL, F. H. 1957. The characterization of pressure-sensitive adhesives. *ASTM Bull.* 221:64.
- WOOD, T. G. 1987. The effects of tackification on waterborne acrylic PSAs. *Adhes. Age* 30:19.
- WRIGLEY, C. W. 1972. The biochemistry of the wheat protein complex and its genetic control. *Cereal Sci. Today* 17:370.

[Received May 13, 1993. Accepted August 14, 1993.]