

Pressure-Sensitive Adhesive Properties of Wheat Flour Dough and the Influence of Temperature, Separation Rate, and Moisture Content¹

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ABSTRACT

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Using the method of reduced variables, probe tack test data on wheat flour-water doughs was shifted into a series of master curves. This illustrated the equivalent influence of increasing temperature, increasing moisture content, and decreasing separation rate on adhesive behavior. An adhesive-cohesive failure transition occurred at 25–30°C (43% moisture content). This transition occurs 50–70°C above the T_g of a pressure-sensitive adhesive and is associated with a shift in viscoelastic behavior from the rubbery state (entanglement network present) to the flow state

(entanglement network disappears due to slippage). Low molecular weight plasticizers (such as water) shift the location of the rubbery-flow state transition to lower temperatures and faster rates. Thus, as the moisture content of the dough increased, the adhesive-cohesive failure transition shifted to lower temperatures and faster separation rates. Processors could prevent cohesive failure, and thus a residue-buildup on equipment, by changing either the formulations or the processing rate-temperature conditions to favor the adhesive side of the failure transition zone.

In the situation where dough sticks to processing equipment, an adhesive bond is formed with the equipment surface. This is analogous to the performance of pressure-sensitive adhesives (PSAs) (Saunders et al 1992). PSAs, like dough, are materials that are viscoelastic under conditions of use (Saunders et al 1992). Both can also be defined as linear amorphous polymers above their glass transition temperatures (Sperling 1992). [Note: The glass transition temperature indicates that amorphous polymers become soft and flexible above this temperature.] An elastomer-resin system controls the viscoelastic properties of PSAs: the elastomer (rubbery polymer) provides an elastic component, while 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 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, while high molecular weight glutenin (elastomeric portion) has been noted as being responsible for the nonadhesive, tough, elastic character of gluten (Ram and Nigam 1983).

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 moduli (G' , a dynamic measure of material elastic stiffness) at low frequencies (bonding time range) are depressed, improving wetting and bond formation. Simultaneously, the high glass transition temperature (T_g) of the low molecular weight resin raises the glass transition temperature of the elastomer-resin system, which in turn elevates the storage moduli (higher forces are required to break the bond) at high frequencies (debonding time range) (Chu 1989). Similarly, wheat flour-water doughs exhibit a low storage modulus in the bonding time range (0.01 rad/sec) and a high storage modulus in the time range for debonding (100 rad/sec) (Navickis et al 1982). Like adhesion scientists, cereal scientists (Wrigley 1972) have also suggested that molecular weight distribution is an important prop-

erty governing the viscoelastic behavior of dough. The elastomeric portion of gluten generally has a broad molecular weight distribution (Kasarda et al 1978), 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.

PSAs are generally formulated with rubbery polymers compounded with tackifiers, fillers, and plasticizers to maintain a balance of peel adhesion, cohesive holding power, and surface tack (Sears and Darby 1982, Butler 1989). The primary property underlying pressure-sensitive adhesion is pressure-sensitive tack. Pressure-sensitive tack is commonly defined as the property that enables a PSA to form a bond of measurable strength immediately upon contact with another surface. Pressure-sensitive tack is primarily governed by the adhesive's rheological properties when interacting with a high energy surface (such as metal).

Both food and adhesion scientists have measured pressure-sensitive tack using a probe tack test. In general, it is conducted by bringing a sheet, block, or film of tacky material into contact with a flat-faced probe. The probe remains there for a specified time and is withdrawn at a constant rate. The maximum separation force or stress during debonding is measured. Others (Bates 1976 and Zosel 1989) have maintained that it is more appropriate to measure tack in terms of the energy of separation per unit area of interface, rather than maximum debonding stress. Knowing sample thickness, probe surface area, and separation velocity, a force-time plot can be transformed into a stress-strain curve. The tack energy is then calculated by integrating the stress-strain curve over the separation period (Zosel 1989):

$$w = \frac{1}{A} \cdot \int F \cdot v \cdot dt = d \cdot \int \sigma \cdot d\epsilon$$

where w = tack energy, A = area of probe, F = force, v = separation velocity, t = time, d = sample thickness, σ = stress = force divided by area, and ϵ = tensile strain = separation velocity multiplied by time divided by sample thickness.

Researchers commonly characterize adhesive materials with single tack values using empirical tests such as the one previously described. However, single tack values vary greatly depending on contact time, contact pressure, and probe material. This occurs because these factors influence bond formation (Hammond 1989). Tack increases with contact time, contact pressure, and probe surface energy, regardless of whether the sample is a PSA or dough (Saunders et al 1992). Adhesive bond strength also changes

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over a continuum of strain rates and temperatures (Gerace 1983). Because pressure-sensitive adhesive polymers (including dough) are viscoelastic, tack values depend on time and temperature; thus, a discrepancy often occurs between laboratory test results and actual adhesive performance (Chu 1989). To resolve this situation, some (Andrianova et al 1968, Kambe and Kamagata 1969, Bates 1976, Dhaliwal et al 1990) have chosen to continue to use the probe tack test, but utilize a wide range of experimental test conditions to characterize adhesive performance under dynamic conditions of use. Such experiments are often difficult to interpret due to the large number of curves generated.

Fortunately, this difficulty in interpretation can be overcome by using the dependency of adhesive polymer viscoelastic properties on time (rate) and temperature to simplify the data. Various PSA scientists (Bates 1976, Tsukatani 1989) have used the method of reduced variables (also known as the time-temperature superposition principle) (Ferry 1980) to successfully shift profiles over the various tack testing conditions into one curve called a "master curve" (Fig. 1). Not only does this manipulation simplify the data, but it also extends the possible range of experimental observational limits beyond values accessible by the instrumentation used to generate the curve. In the study of doughs, this methodology has been successfully applied to data obtained over a limited temperature and moisture range in transient and dynamic rheological testing (Cunningham and Hlynka 1954, Hibberd and Wallace 1966). The method of reduced variables is based on the fact that different variables (such as temperature, time [rate], plasticizer concentration, and stress intensity) can have equivalent or analogous effects on the acceleration of processes involved in molecular relaxation or rearrangement (Sichina 1988, Rajeckas 1989). For example, increasing temperature and decreasing strain rate have equivalent effects on the mechanical properties of polymers. Bates (1976) and Tsukatani et al (1989) were able to produce a master curve from probe tack and pulling cylinder test data. They confirmed Ferry's (1980) observation that the complicated aspects of mechanical behavior (such as peel or tack) depend on the same molecular motions that determine viscoelastic relaxation times. In addition to studying characteristic probe tack values over a wide range of experimental conditions, it is also important to note whether adhesive bond failure during the measurement of tack is cohesive (residue is left on adherend) or adhesive (adhesive cleanly separates from adherend). For instance, it may be acceptable for a food material to exhibit tack, as long as it exhibits adhesive failure when pulled from processing equipment (has sufficient cohesive strength). Rudolph and Tscheuschner (1979) noted that in dough, separation was achieved either by a flow process or fracture, depending upon rate of separation. They also noted that adhesive separation was rarely completely achieved (no residue left on contact surface). Usually, tiny amounts of dough could be seen remaining on the contact surface even when failure was interfacial. PSA scientists have discovered that the mode of failure is dependent upon separation rate and temperature, while cereal scientists have recognized it as a function of separation rate and moisture content. Both have observed a transition zone from adhesive to cohesive failure, where the mode of failure is not consistent. Like pressure-sensitive tack, cohesive strength (therefore, mode of failure) of the adhesive is determined by polymer viscoelastic properties.

Since the same rheological criterion governing the loss of tack in PSAs applies to flour-water dough (Heddleson et al 1993), it can be assumed that viscoelastic behavior is the predominant factor controlling flour-water dough tack to high energy surfaces (metal). The first objective of this study was to show whether tack depends on the same molecular motions determining viscoelastic relaxation times. If so, probe tack test data over various ranges of temperature, separation rate, and dough moisture content could be simplified using the method of reduced variables. This study also sought to use a new measure of adhesive-cohesive failure—the weight of residue left on the probe surface after tack testing—to quantify how the adhesive-cohesive failure transition was influenced by temperature, separation rate, and dough moisture content.

Flour

Wheat flour was supplied by Nabisco Brands, Inc. (Toledo, OH). The flour was a commercial blend of different cultivars having 8.8% protein, 0.45% ash, and 13.0% moisture (AACC 1983).

Test Sample Preparation

Doughs were mixed in the 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 varied over three levels: 41, 43, and 45% (45.3, 50.4, and 55.8% absorption, respectively) as needed. 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 environmental 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 (UTM) (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 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 mm × 1.25 mm × 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 UTM crosshead. A stainless-steel collar was secured

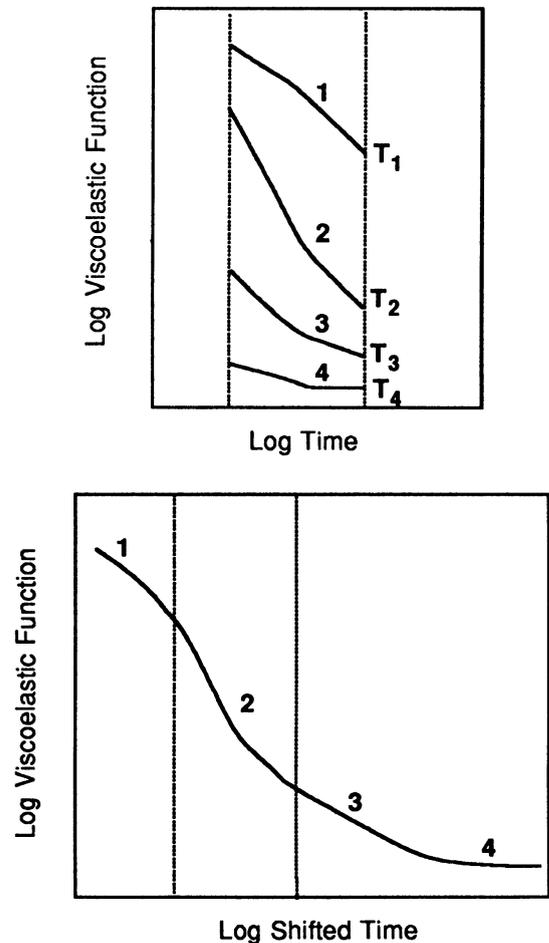


Fig. 1. A generalized time-temperature master curve. Temperature effect is evaluated by a horizontal shift of the log viscoelastic function curves along the log time axis (Rajeckas 1989). T_1 – T_4 are four different levels of temperature.

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 mm × 25 mm) strips of polyethylene (1 mil) to prevent surface-drying during the 30-min period required to equilibrate the test sample to the required test temperature. 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 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).

Adhesion Measurements

Once sample preparation was complete, a probe tack test apparatus (Heddleson et al 1993) was attached to the UTM and located within the environmental chamber.

A computer program in BASIC (Heddleson 1994) was developed to automate the test procedure and calculate probe tack, tack energy, and probe residue. Before conducting a probe tack test, the program required the following input: test material, contact time, deformation rate, full-scale force, separation rate, probe type, contact force, sample height, probe tare weight, and test temperature-relative humidity. After the 30-min temperature equilibration period, 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 was quickly removed. The sample was positioned underneath the probe and the test was started via the computer. After starting the test, the computer signaled the UTM 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. During the contact time, the operator manually changed the UTM crosshead speed to the appropriate withdrawal rate. The computer then signaled the UTM to raise the probe from the sample at a given withdrawal rate, generating the debonding portion of the curve. After testing was completed, the computer program required an input of a qualitative judgment (visual observation) of failure type and probe weight after testing to calculate "probe residue", a quantitative indication of failure type. The probe was removed immediately from the probe holder and weighed on an

analytical scale (model AE200, Mettler, Hightstown, NJ). The visual observation was recorded as a *C* for cohesive failure or an *A* for adhesive failure. The weight of material left on the probe after testing was entered in grams. Probe residue was removed with water between tack tests. Three measurements were calculated by the computer: probe residue (*g*), the amount of dough left on the probe after testing; probe tack (*N*), the maximum force of the debonding curve; tack energy (μJ), the area under the debonding curve.

For generation of the separation rate-temperature master curve data, two independently mixed dough samples were tested at 43% total moisture using three different constant temperatures (25, 35, and 45°C), and at each of the separation rates once as follows on each dough: 10, 50, 200, 500, and 1,000 mm/min. The same data collection procedure was implemented for the generation of separation rate-moisture content master curves, however the tests were run at 35°C using three different constant total moisture contents (41, 43, and 45%). These ranges were selected on the basis of their representation of "normal" use ranges, their good fit within equipment control limitations, and their avoidance of any drastic viscoelastic transitions (Heddleson et al 1993).

For generation of temperature-moisture master curve data, two independently mixed dough samples were tested at a 200 mm/min separation rate using a combination of three levels of moisture content (41, 43, and 45%) and five temperatures (25, 30, 35, 40, 45°C). Six repetitions of the tack test were done per dough per moisture content-temperature combination.

All data for master curves was gathered holding the other tack test variables constant: copper probe with a 20 mm diameter and a 0.8 μmm surface finish, 50 mm/min deformation rate, 5 sec contact time, and 99.69 g contact force (3,111 Pa contact stress).

Method of Reduced Variables

To prepare the master curves for the separation rate-temperature superposition of probe tack test parameters, the log separation rate was plotted on the horizontal axis, while the log of a specific probe tack test parameter (probe tack, tack energy, or probe residue) was plotted on the vertical axis. One transparency sheet was used per temperature. Using the 35°C/43% total moisture probe tack curve as a reference curve, data on the other sheets were superimposed and shifted horizontally along the rate axis until the best alignment of the data points in the regions of overlap between adjacent sheets was achieved. Two shift factors (a_T), the factors by which relaxation rates have been changed, were calculated by subtracting the log separation rate at an overlapped data point on the reference curve (35°C) from the log separation rate at an overlapping data point (25°C or 45°C). The shift factors, tabulated for each superposition, are shown in Table I. A shift factor of zero indicates the reference curve. When the shift factor is negative, the associated curve is shifted to the right side of the reference curve. When the shift factor is positive, the associated curve shifts to the left side of the reference curve. Using the shift factor, new separation rates can be calculated for each temperature resulting in one continuous curve (master curve) by subtracting the shift factor from each log separation rate. This general procedure was repeated for the other superpositions, and lines were

TABLE I
Shift Factors for Master Curves

Master Curve	Temperature (°C)	Separation Rate (mm/min)	Moisture Content (%)	Log Shift Factor		
				Probe Residue	Probe Tack	Tack Energy
Separation Rate-Temperature	25		43	-1.00	-0.40	-0.70
	35		43	0	0	0
	45		43	1.30	0.30	0.60
Separation Rate-Moisture Content	35		41	-1.30	-0.70	-0.70
	35		43	0	0	0
	35		45	0.70	0.30	0.40
Temperature-Moisture Content		200	41	0.18	0.05	0.26
		200	43	0	0	0
		200	45	-0.15	-0.18	-0.07

drawn through the master curve data points using a reasonable visual fit.

Reliability of master curve data was verified using control tests. Control tack tests were run at specific separation rates and temperatures between and beyond the data used to construct the separation rate-temperature, separation rate-moisture content, and temperature-moisture content master curves. For the separation rate-temperature and separation rate-moisture content master curves, control test data points were run using 43% moisture content, 35°C, and varying the separation rate at: 5, 20, and 100 mm/min. For the temperature-moisture content master curve, control test data points were run using a 43% moisture content, a separation rate of 200 mm/min, and varying the temperature at: 16, 28.5, and 55°C. Control test data points were plotted directly onto the master curve. The final step was to establish the degree of fit of the control data points to the master curve. The degree of experimental error associated with these control values is shown in Table II.

RESULTS AND DISCUSSION

Figures 2-7 indicate that separation rate-temperature, separation rate-moisture content, and temperature-moisture content

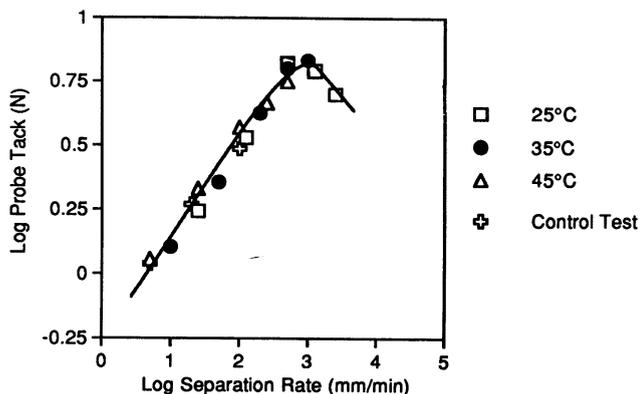


Fig. 2. A separation rate-temperature master curve of flour-water dough for probe tack. Dough moisture content was held constant at 43%.

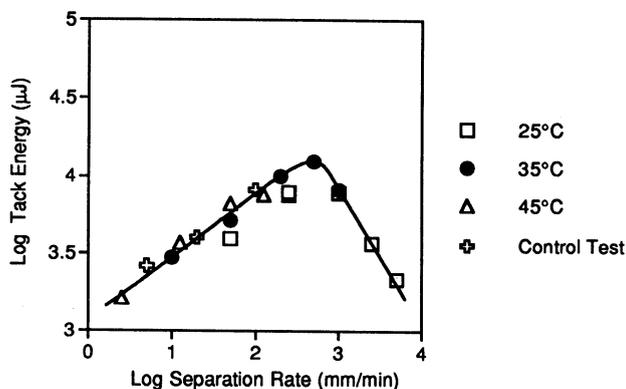


Fig. 3. A separation rate-temperature master curve of flour-water dough for tack energy. Maximum occurs at a 500 mm/min separation rate. Dough moisture content was held constant at 43%.

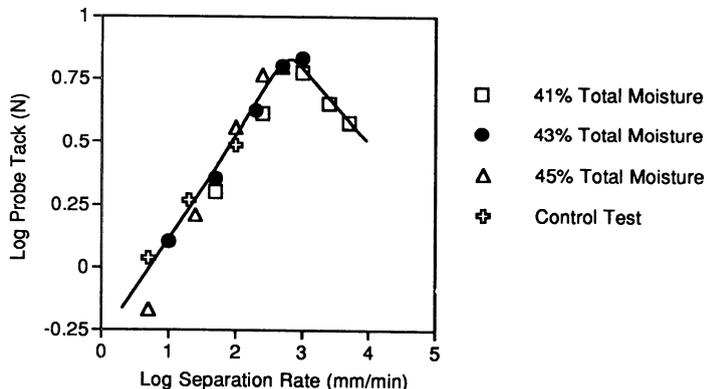


Fig. 4. A separation rate-moisture content master curve of flour-water dough for probe tack. Dough temperature was held constant at 35°C.

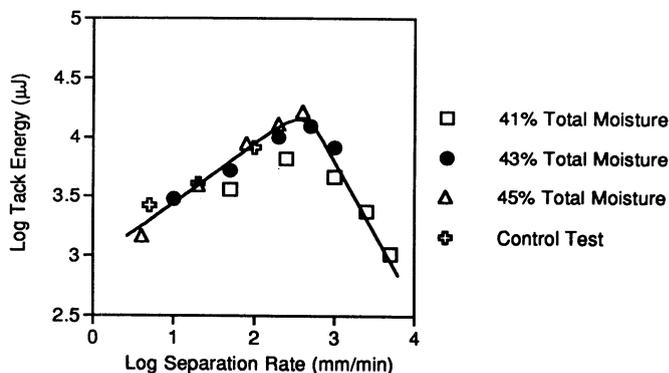


Fig. 5. A separation rate-moisture content master curve of flour-water dough for tack energy. Maximum occurs at a 500 mm/min separation rate. Dough temperature was held constant at 35°C.

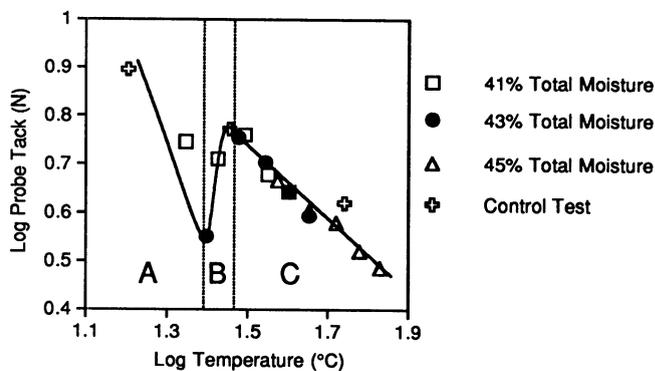


Fig. 6. A temperature-moisture master curve of flour-water dough for probe tack. Regions A, B, and C = adhesive failure, adhesive to cohesive failure transition zone, and cohesive failure, respectively. Separation rate was held constant at 200 mm/min.

TABLE II
Coefficient of Variation (%) Data for Master Curve Control Points

Master Curve	Temperature (°C)	Moisture Content (%)	Separation Rate (mm/min)	Coefficient of Variation, %		
				Probe Residue	Probe Tack	Tack Energy
Separation Rate-Moisture Content/ Separation Rate-Temperature	35	43	5	0.8	2.0	22.0
	35	43	20	2.4	1.5	3.0
	35	43	100	2.9	3.7	3.0
Temperature-Moisture Content	25	43	200	0.0	14.3	28.0
	35	43	200	98.3	4.6	22.0
	45	43	200	7.0	10.2	12.0

analogies successfully apply to the complex mechanical behavior of probe tack in wheat flour dough. The positive values of shift factors at 45°C (separation rate-temperature master curve) and 45% moisture content (separation rate-moisture content master curve) (Table I) indicate an increase in dough temperature or moisture content shifts the curve to the left; the same effect could be achieved by reducing the separation rate. In other words, increasing temperature or moisture has the same effect on tack properties as decreasing the separation rate. This interpretation was confirmed by conducting control tests at slow separation rates to allow interpolation within the range of experimental separation rates and extrapolation below the slowest rate of the original series. The location of the interpolated control data points, and even the extrapolated points, are in excellent agreement with the calculated master curves. Most control values had reasonable experimental variation, especially since the probe tack test involves failure, a highly variable process.

The separation rate-moisture content shifting procedure created a curve that spanned a greater range of separation rates than did separation rate-temperature shifting. This indicates moisture content had a greater influence on probe tack than did temperature, within the tested experimental ranges. The shift factors in Table I illustrated that shifting from the highest level of moisture content or temperature to the reference condition (35°C or 43% moisture content, respectively), resulted in the same shift in rates. However, the effect of shifting to the lowest moisture content was greater than the effect of shifting to the lowest temperature within the limited test range. This was not surprising, given the test range (16–55°C) was in a region well above the temperature interval of 20°C above the relevant glass transition temperature (T_g' , the subzero T_g of any system with enough water to allow ice to form below 0°C) of the dough (Levine and Slade 1990,

Slade and Levine 1991).

Figure 6 illustrates a temperature-moisture content analogy for probe tack. The negative values of shift factors at 45% moisture content (Table I) indicate an increase in moisture content shifts the curve to the right. This confirms the results of the separation rate-temperature and separation rate-moisture content probe tack master curves: increasing temperature has the same effect on tack properties as increasing moisture content of the dough. This master curve indicates a strong transition region (region B, between 25–30°C) not present in the previous probe tack master curves because it contains a control data point (16°C) that is closer to the T_g' of the dough system. Upon first examination of the data points, it would be tempting to regard the 25°C/43% total moisture data point as an outlier. However, a temperature-moisture analogy for probe residue (Fig. 8) shows a sharp transition at exactly the same temperature region as the probe tack master curve (Fig. 6). Not surprisingly, this region of transition also contained a control point (28.5°C) with an extremely high coefficient of variation (Table II). Figures 8–10 are a quantitative representation of cohesive failure (failure within the bulk of the material, occurring at higher temperatures-moistures and slower separation rates, resulting in residue remaining on the probe after testing) and adhesive failure (failure at the interface of the adherend, occurring at lower temperatures-moistures and faster separation rates, usually leaving none or barely measurable amounts of residue on the probe). Comparing Figures 6 and 8, probe tack decreases with increasing temperature, bond failure is adhesive, and a barely measurable amount of residue is left on the probe after separation in region A. In region B, probe tack increases and amount of residue left on the probe after separation increases with temperature. Probe tack then decreases, cohesive bond failure occurs, and the amount of residue left on

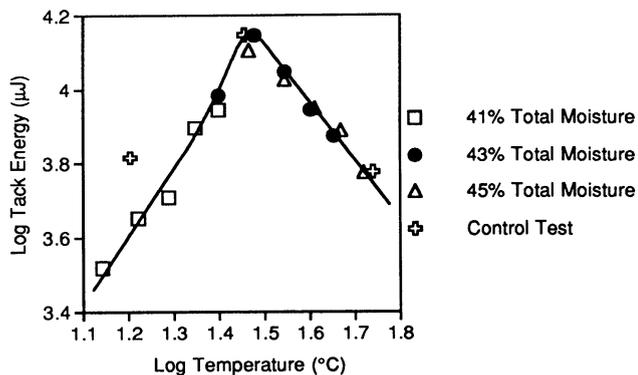


Fig. 7. A temperature-moisture content master curve of flour-water dough for tack energy. Maximum occurs at 30°C. Separation rate was held constant at 200 mm/min.

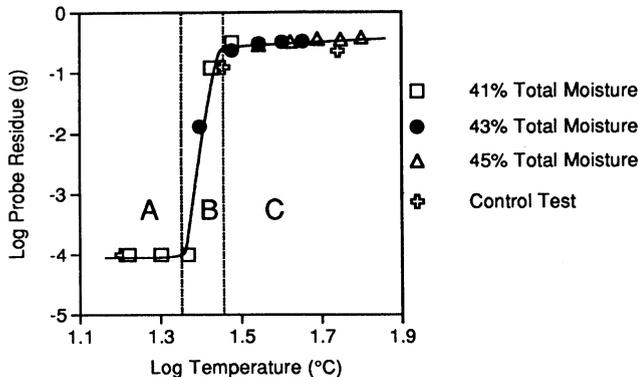


Fig. 8. A temperature-moisture content master curve of flour-water dough for probe residue. Regions A, B, and C = adhesive failure, adhesive to cohesive failure transition zone, and cohesive failure, respectively. Separation rate was held constant at 200 mm/min.

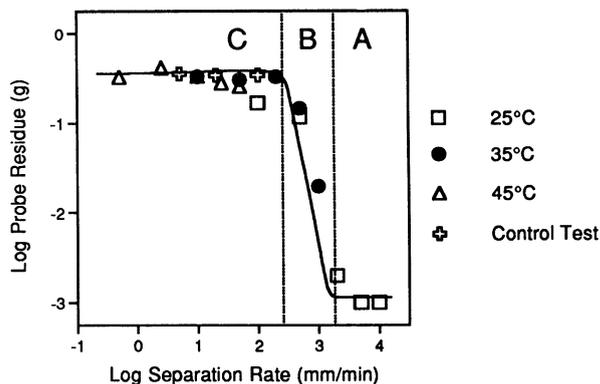


Fig. 9. A separation rate-temperature master curve of flour-water dough for probe residue. Regions A, B, and C = adhesive failure, adhesive to cohesive failure transition zone, and cohesive failure, respectively.

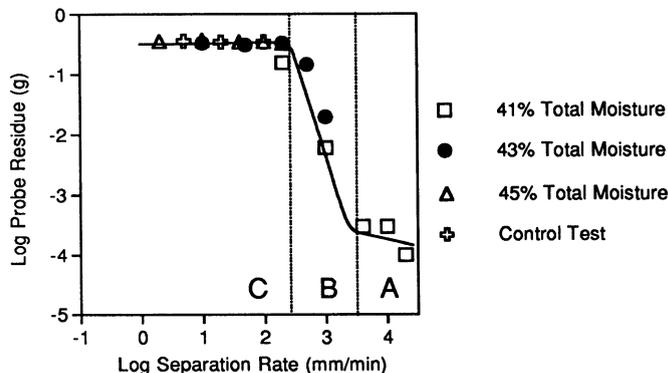


Fig. 10. A separation rate-moisture content master curve of flour-water dough for probe residue. Regions A, B, and C = adhesive failure, adhesive to cohesive failure transition zone, and cohesive failure, respectively.

the probe after separation is constant in region C. These results are supported by the temperature-moisture content analogy for tack energy (Fig. 7), which also indicated a maximum in the same range of temperature as the adhesive-cohesive failure transition region.

The influence of moisture content and separation rate on the existence and nature of the adhesive-cohesive failure transition in flour-water doughs was previously noted on a visual basis by Rudolph and Tscheuschner (1979) and Pshenishniuk et al (1981). Many PSA investigators have found similar trends in other types of PSAs (Aubrey and Sherriff 1980, Good and Gupta 1988). PSA scientists have recognized a generalized curve (Fig. 11) showing peel force undergoing a continuous decrease (region A) where the mode of failure is adhesive. In region B, a transitional period takes place within a narrow temperature range where the mode of failure changes from adhesive to cohesive. As temperature continues to increase, peel force again decreases (region C) where cohesive failure occurs. The shape of this generalized curve is very similar to that of the master curve (Fig. 6) associated with the temperature-moisture content analogy in this study, especially when the control point at 16°C/43% total moisture is added to the master curve.

At temperatures $>20^{\circ}\text{C}$ above T_g' , the viscoelastic behavior of polymers is determined by their entanglement network (Zosel 1989). The presence of an entanglement network is reflected by the presence of a maximum in the master curve (Ferry 1980). Zosel (1989) observed that this maximum occurs 50–70°C above the T_g of linear, amorphous PSA polymers. The general consensus of both adhesion and cereal scientists is that the adhesive-cohesive failure transition is associated with a shift from the rubbery state to flow state transition (Kaelble 1969, Rudolph and Tscheuschner 1979, Pshenishniuk et al 1981, Satas 1989). [Note: Figure 4 exhibits a maximum in region A and another in region B. The maximum in region A, occurring at a lower temperature closer to T_g' reflects the underlying glass state-rubbery state transition, while the maximum in region B is associated with the rubbery state-flow state transition.] During slower separation rates (higher temperatures-moisture contents), relaxation processes have time to occur in the macromolecules of the dough biopolymers. The rate of entanglement slippage exceeds the rate of adhesive deformation (Kaelble 1969), resulting in cohesive failure of the material, which behaves as a liquid. The maximum in probe tack values, which coincides with the onset of cohesive failure, reflects the additional work of disentanglement (Kaelble 1969). At higher separation rates, lower temperatures and moisture contents, relaxation processes do not have time to begin. Chain segments are restricted from moving by an entanglement network, the material behaves as a solid, and adhesive failure of the material results (Kaelble 1969).

Addition of a low molecular weight diluent or plasticizer (such as water) to a high molecular weight polymer (dough biopolymers) shifts the location of the rubbery state to lower temperatures (Ferry 1980). Subsequently, the position at which entanglements slippage begins (cohesive failure) shifts as well. This behavior has been shown in PSAs by Aubrey and Sherriff (1980). Based on this information, it would be expected that as water content of the dough increases, the position at which cohesive failure begins would shift to lower temperatures. Figure 12 illustrates this observation. At moisture content of 41 and 43%, cohesive failure begins to occur at 35 and 25°C, respectively. It may be inferred that cohesive failure begins to occur for the 45% moisture content dough at a temperature well below 25°C. Equivalently, addition of a low molecular weight diluent or plasticizer would cause the rubbery state to shift to shorter times or faster rates (Fig. 9). Thus, as water content of the dough increases, the position at which cohesive failure begins would shift to faster separation rates. Figure 13 illustrates this point. At moisture contents of 41 and 43%, cohesive failure begins at a 50 and 200 mm/min separation rate. For a dough with a 45% moisture content, it may be inferred that cohesive failure would begin at a separation rate greater than 1,000 mm/min.

When adherence of a food material is undesirable, it is usually

because the material has failed cohesively and left a residue that continues to build up on the equipment over time. An extreme solution to this situation is to raise the storage modulus to $>10^5$ Pa, so that tack is zero (Heddleson et al 1993) and adhesive failure occurs. However, the rheological criterion necessary for this adhesive behavior may not be suitable for conditions required in later processing steps. This study has shown that it is possible, via alteration of PSA composition or temperature and rate conditions, to reach a point where tack still occurs, but an insignificant amount of residue is left on a metal surface. It is important to recognize that the adhesive-cohesive failure transition is dependent upon the location of the rubbery state-flow state zone, whose

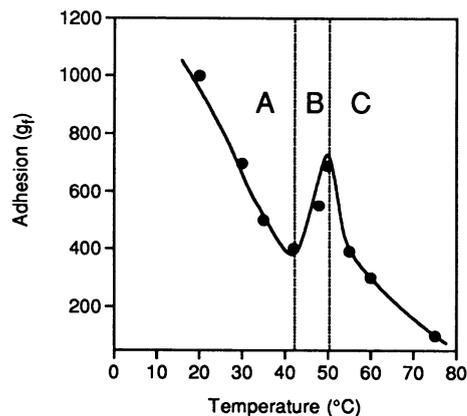


Fig. 11. A generalized curve showing the dependence of adhesion in grams-force on temperature. Regions A, B, and C = adhesive failure, adhesive to cohesive failure transition zone, and cohesive failure, respectively (Satas 1989).

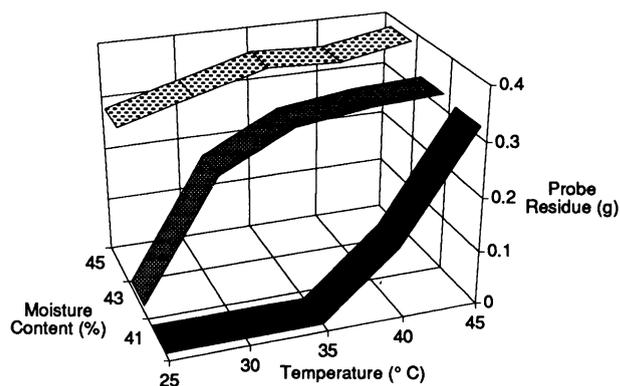


Fig. 12. Increasing dough moisture content results in shifting the adhesive-cohesive failure transition zone to lower temperatures. Separation rate was held constant at 200 mm/min.

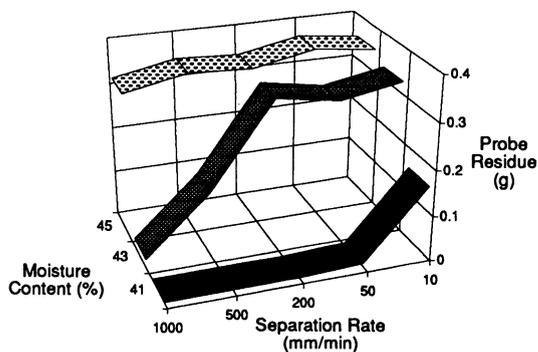


Fig. 13. Increasing dough moisture content results in shifting the adhesive-cohesive failure transition zone to faster separation rates. Dough temperature was held constant at 35°C.

location in turn is highly sensitive to plasticizer or diluent (water) concentration. A suitable goal for processors would be to ensure that either the formulation or processing rate-temperature conditions remain on the adhesive side of the failure transition zone.

CONCLUSION

Probe tack test data obtained over various temperatures, dough moisture contents, and separation rates can be converted by the method of reduced variables into a series of separation rate-temperature, separation rate-moisture content, and temperature-moisture content master curves. Increasing temperature or moisture content has the same effect on tack properties as decreasing the separation rate. Maxima in the probe tack and tack energy master curves (known to occur 50–70°C above T_g) indicated the presence of an entanglement network in the dough. Both probe tack temperature-moisture content and probe residue separation rate-temperature, separation rate-moisture content, and temperature-moisture content master curves displayed a transition zone where failure type changed from adhesive to cohesive. It is generally agreed that this transition zone is associated with a shift from the rubbery state (where an entanglement network is present) to the flow state (where the entanglement network disappears due to slippage). Addition of a low molecular weight diluent or plasticizer (such as water) to a high molecular weight polymer (such as dough polymers) shifts the location of the rubbery plateau to lower temperatures and shorter times (faster rates) (Ferry 1980). Thus, as the moisture content of the dough increased, the adhesive-cohesive failure transition shifted to lower temperatures and faster separation rates (shorter times).

It is important to recognize that the adhesive-cohesive failure transition is dependent upon the location of the rubbery state-flow state zone, whose location is highly sensitive to plasticizer or diluent (water) concentration. A suitable goal for processors would be to ensure that either the formulation or processing time and temperature conditions remain on the adhesive side of the failure transition zone. This would allow adhesion to occur but prevent residue left by cohesive failure from accumulating on processing equipment.

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