Macromol. Symp. ***140,*** *125–135 (1999)*

Effect of Glass Transitions on the Rheological Properties of Food Polymers

Victor T. Huang

Pillsbury Company, Minneapolis, MN, USA

SUMMARY: The rheological properties of food products are highly dependent on the physical state of the structural matrix, which ranges from the glassy state, the glass-rubber transition region, the rubbery plateau region, the rubbery flow region, and viscous flow region. Depending upon the combination of temperature and/or moisture content, the viscosity could be anywhere from 10^{15} mPa.s for glassy material and 1 mPa.s for flowable, low viscosity liquid. During the glass transition range alone, the rheological properties can change as large as 1000 times. The rheological properties of ingredients, in-process intermediates, and finished products also affect the processing techniques, textural quality, physical and chemical stability during storage. In this paper, the similarity in rheological behaviors between synthetic and food polymers, as affected by degree of crystallinity, cross-linking, plasticization, and phase separation is reviewed. Various mathematical equations for modeling the changes in rheological properties during glass transitions are also discussed. The advantages and shortcomings of each model will also be compared.

Introduction

It was not until the early 80's that food scientists, pioneered by Drs. Harry Levine and Louise Slade, realized that synthetic polymer principles are applicable to food systems[1-8)]. Various thermal analysis techniques have been used to demonstrate the similarity between those two systems[9-11)]. In this review, the rheological comparisons will be on (1). the ranges of modulus changes and temperature spreads during glass transition and the effects due to crystallinity, cross-linking, plasticization, and phase separation; (2) various models describing the rheological changes at and around T_g, such as Williams-Landel-Ferry(WLF), Vogel-Tammann-Fulcher(VTF), Power-law, or Peleg-Fermi equations.

CCC 1022-1360/99/$ 17.50+.50/0

Comparison between synthetic and food polymers

Glass transition temperature(T_g) is a function of product composition, molecular weight of the continuous structural matrix, degree of branching, degree of crosslinking, crystallinity, and degree of plasticization. Figure 1 shows the five regions of viscoelasticity of a synthetic polystyrene: AB glassy region, BC glass transition region, CD rubbery plateau region, DE rubbery flow region, and EF viscous flow region[12)]. The modulus-temperature curve is very sensitive to many structural factors such as molecular weight, degree of cross-linking, % crystallinity, copolymerization, plasticization, and phase separation.

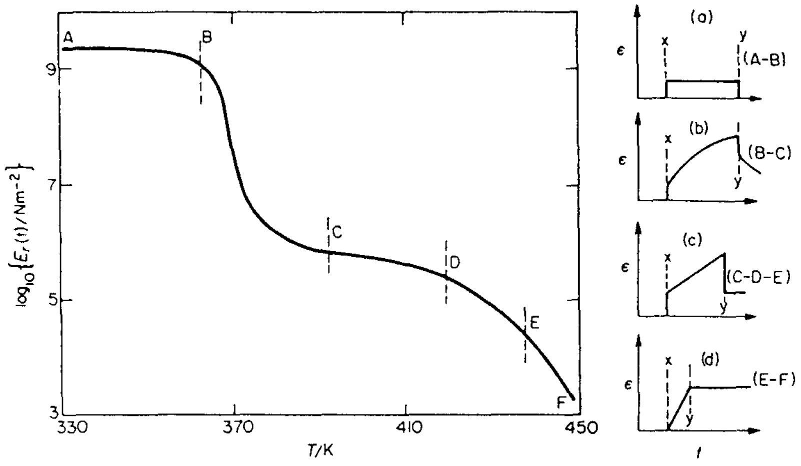

Fig.1: Five regions of viscoelasticity, illustrated by using a polystyrene sample. Also shown are the strain-time curves for stress applied at x and removed at y:(a) glassy region;(b) leathery state;(c) rubbery state; and (d) viscous state (From Ref. 12).

For un-crosslinked molecules, the drop in modulus is about three decades during glass transition. As the degree of cross-linking increases, the drop in modulus during glass transition decreases. For example, in Figure 2, for a gluten sample equilibrated in 65% Relative Humidity (RH), the drop in modulus is less than 2 decades[13)]. The degree of viscosity drop at a constant $T-T_g$ has been used as an index of "fragility". Organic glass usually is more fragile than inorganic glass. High crystallinity sample has lower modulus drop at T_g due to the reduced amount of amorphous region, and has higher T_g. Plasticizers decrease both T_g and rubbery modulus of PVC-diethylhexyl succinate system

(Figure 3[14]) while Figure 4 shows that water is a powerful plasticizer for gluten. Crispy breakfast cereal is in glassy state (10^9 Pa)[13]. Glucose glass is $8*10^9$ Pa, while glucose/sucrose glass with 2-3% moisture is $8*10^8$ Pa[15]. Shortening and emulsifiers do not affect T_g, but they decrease the rubbery modulus[16].

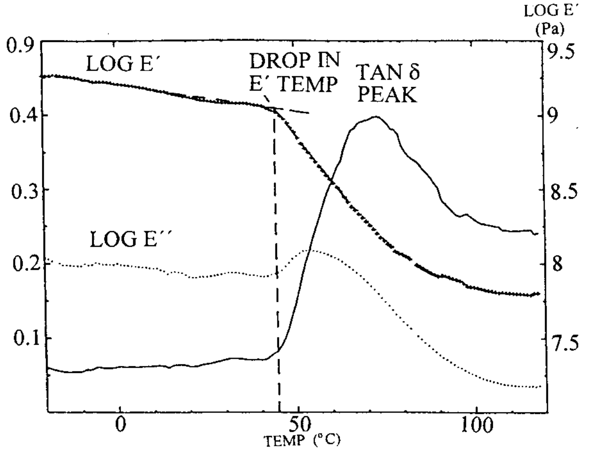

Fig. 2: A typical DMTA plot for gluten (RH = 65%), showing tanδ, log loss modulus (E") and log elastic modulus (E') as a function of temperature (From Ref. 13).

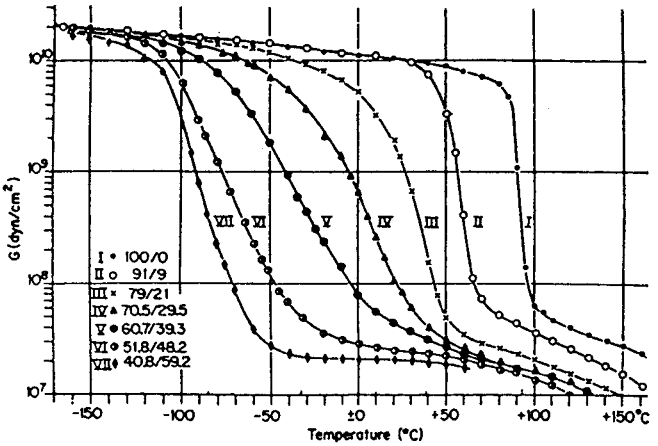

Fig. 3: Dynamic shear modulus of polyvinyl chloride plasticized with various amounts of diethylhexyl succinate plasticizer (From Ref. 14).

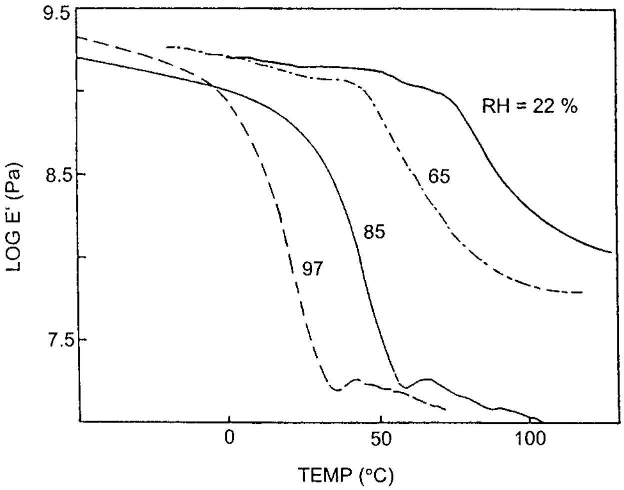

Fig. 4: DMTA plot for gluten samples stored under different RH values (From Ref. 13).

The length of the rubbery plateau is a function of molecular weight and the number of entanglement per molecule. Thus, as shown in Figures 2 and 5, gluten sample at 65% RH, due to its high molecular weight and degree of entanglement, has very long rubbery plateau while sorbitol almost does not have a visible one17). Sorbitol goes right into rubbery and viscous flow right after glass transition region, but gluten does not have the rubbery flow and viscous flow regions, which is probably due to its relatively high degree of cross-linking and/or entanglement. Molasses and batter are examples of food systems in viscous flow regions at room temperature. Microwave heated bread is in between the glass transition and rubbery plateau regions as typified by its leathery-rubbery texture (10^6 to 10^7 Pa). Cheese and bread dough are in rubbery flow region at room temperature (10^4 to $5*10^5$ Pa).

A blend of incompatible synthetic polymers will phase-separate and show more than one T_g, as indicated in Figure 6 for sodium caseinate-water and fructose-water systems16). In a polymer with crystallizable plasticizer, one can detect both the glass transition of the maximally freeze-concentrated polymer-plasticizer matrix and the melting of the plasticizer. As shown in Figure 7 for the sucrose-water and PVP-water systems17). The figure also shows that higher molecular weight compound gives higher T_g'.

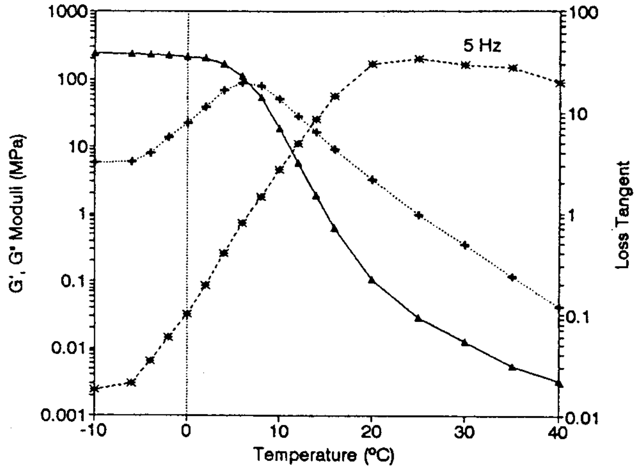

Fig. 5: Annular shear test for amorphous sorbitol: (Δ) storage modulus G', (+) loss modulus G", and (*) loss tangent (From Ref. 15).

Air behaves as a diluent and is effective in edifying some products, such as breakfast cereals, which would otherwise be too hard. Gas cells inside some products can be from many sources: yeast leavening, chemical leavening, injected inert gases, carbon dioxide, ethanol. Those gas cells will eventually have the same gaseous composition as that of the packaged environment. One area that differs from synthetic polymer system is the presence of fat in food matrices. Fats and emulsifiers do not affect T_g, but do decrease the rubbery modulus[18)]. The tenderizing effect at serving temperature is a function of the solid fat index, fat content, and fat crystalline form. Fats and emulsifiers also enhance perceived moistness to bakery products. This is why fat-free bakery products usually taste dry and not as tender. From all these observations, we can conclude that indeed food systems can be viewed as polymer systems.

Models for describing rheological changes around T_g

Basically, there are two ways for modeling the viscosity/modulus changes around Tg. The VTF[19)], Power-law[20)], and WLF[21)] models start in the rubbery flow or plateau regions, using viscosity, interpolating toward the glassy region while the Peleg-Fermi model starts from glassy

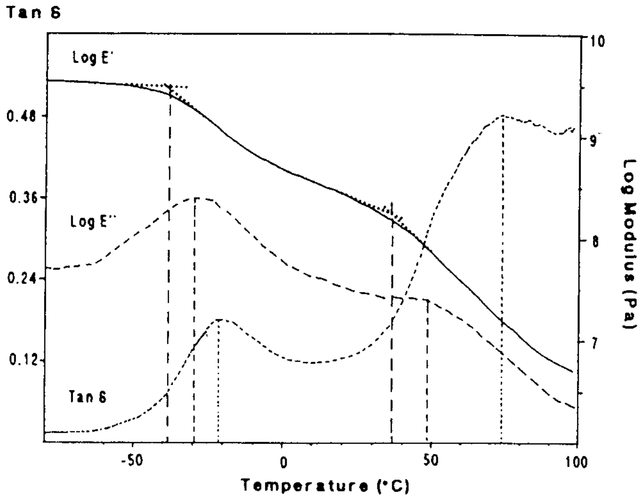

Fig. 6: DMTA plot of sodium caseinate and fructose at a ratio of 2:1 stored at 75% RH (16% water)(From Ref. 16).

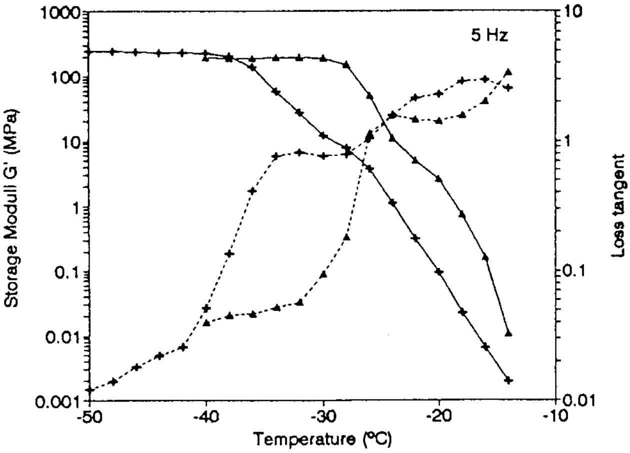

Fig. 7: Annular shear test for frozen 50% sucrose (+) and PVP (Δ) solutions; full line: storage modulus G', dotted line: loss tangent (From Ref. 15).

state, using modulus, increasing in temperature toward the rubbery plateau region. These models are listed below:

VTF model

$\eta = A\exp[B/(T-T_1)]$ or $\eta = A\exp[D^*T_1/(T-T_1)]$

where T_1: the temperature of viscosity divergence

D : strength parameter

Power-law model

$\eta = C(T-T_2)^r$

where $r<0$.

WLF model

$\log(\eta/\eta_o) = -C1(T-T_o)/(C_2+T-T_o)$

where η_o is viscosity at T_o

Table 1 listed coefficients for various models as measured for glucose and fructose samples[22]. The problem associated with these models is that those coefficients for all food ingredients are not readily available in the literature, and it takes lots of effort to determine those values even just for one compound. Thus, it is very difficult to establish the relationship between structure and functionality among food ingredients. In Vogel-Tammann-Fulcher model, the higher the D value, the thicker the viscosity will be at a constant temperature above Tg, which implies that products with high D values are expected to be more stable at a given temperature above Tg. Products with higher Tm/Tg ratio tends to have this superstructuring effect.

Peleg-Fermi model[23]

Fermi distribution function describes a normalized distribution of y ranges from 0 to 1 as a function of T with midpoint at T_o and the spread factor "a" which defines the shape of the curve. Initially, Peleg [23-24] adapted it to describe the temperature dependency of G'. When $T=T_o$,

Table 1: Application to glucose and fructose[22]

models	coefficients	glucose	fructose
Vogel-Tammann-Fulcher			
$\mu = A \exp[B/(T-T_1)]$	A(Pa.s)	$2.98*10^{-6}$	$3.44*10^{-7}$
	B(K)	1926	2391
	T_1(K)	256	227
	T_g(K)	304	283
Power-law			
$\mu = C(T-T_2)^r$	C(Pa.s)	$8.07*10^{22}$	$3.36*10^{22}$
	r	-11.4	-11.1
	T_2(K)	298	280
	T_g(K)	307	289
Williams-Landel-Ferry			
$\log(\mu/\mu_o) = -C_1(T-T_o)/(C_2+T-T_o)$	μ_o(Pa.s)	$3.55*10^{11}$	$4.37*10^{11}$
	$C_1(K^{-1})$	17.44	
	C_2(K)	51.6	
	T_o(K)	304	286

G value is only 50% of G_o. The general equation is $G'(T) = G_o/\{1+\exp[(T-T_c)/a]\} + G_r$ where G_o is G' value in glassy state; T_o is the midpoint of change from G_o to G_r; a is the spread factor. The temperature variable can be replaced with moisture content or water activity while E' can replace G'. For example,

$E'(T) = E_o/\{1+\exp[(T-T_c)/a]\} + E_r$

$G'(M) = G_o/\{1+\exp[(M-M_c)/b]\} + G_r$

$G'(a_w) = G_o/\{1+\exp[(a_w-a_{wc})/c]\} + G_r$

where T is temperature, M is moisture content and a_w is water activity.

It would be interesting to define the critical G' or E' for a given system below which the textural properties such as crispness becomes unacceptable. Peleg further expanded the model into simultaneous temperature and moisture dependency of G' as

$G'(T,M)= G_o/\{1+\exp[(T-T_c(M))/a(M)]\} + G_r(M)$.

In this case, the following 2 equations which have a lot of coefficients need to be derived first,

$T_C(M) = T_{CO}*\exp^{-k_1*M}$ and $a(M)= a_O*\exp^{-K_2*M}$

The advantage of the Peleg-Fermi model is that it covers the ranges of modulus at and around glass transition. However, similar problem to the other models, we need more data on different ingredient systems in order to establish the relationship between the spread factor, modulus change, and molecular structure.

Conclusion

Rheological changes during glass transition are similar for synthetic and food polymers. However, rubbery flow and viscous flow regions are not as easy to detect for food systems, this might be due to inherent molecular cross-linking, or due to decomposition or moisture loss at high measurement temperatures. In general, food systems have broader transition due to compositional or phase heterogeneity. Rubbery modulus of food macromolecules may be modified by emulsifiers, shortenings, water, or other low molecular weight plasticizers. Superstructuring effect with respect to temperature and plasticizer needs further study before it can be used for food system stabilization. Rheological changes can be mathematically described by various models. For each model, various coefficients of food systems needed to be established.

References

1) L. Slade, H. Levine, “Recent advances in starch retrogradation”. In “Industrial Polysaccharides”, eds. Stivala,S.S., Crescenzi,V., Dea,I.C.M. Gordon & Breach, 1986.

2) L.Slade,H. Levine, J.W. Finley. “Protein-Water Interactions: Water as a Plasticizer of Gluten and other Protein Polymers”. In “Protein Quality and the Effects of Processing”, eds. RD Phillips and JW Finley, Marcel Dekker, New York 1988, p. 9-124

3) H. Levine, L. Slade. Influence of the Glassy and Rubbery States on the Thermal,

Mechanical, and Structural Properties of Doughs and Baked Products. In H Faridi, JMF Faubion, eds. Dough Rheology and Baked Product Texture. Van Nostrand Reinhold, New York 1989, p. 157-330

[4] L. Slade, H. Levine. Beyond Water Activity:Recent Advances Based on an Alternative Approach to the Assessment of Food Quality and Safety. CRC Crit. Revs. Food Sci. Nutr. **30**(2-3): 115-360 (1991)

[5] H. Levine, L. Slade. Water Relationships in Foods. New York:Plenum Press, 1991.

[6] H. Levine, L. Slade. Glass Transitions in Foods, in Physical Chemistry of Foods, eds. Schwartzberg and RW Hartel, Marcel Dekker, New York 1992, p. 83-221

[7] L. Slade, H. Levine, J Ievolella, M Wang.. The Glassy State Phenomenon in Applications for the Food Industry: Application of the Food Polymer Science Approach to Structure-Function Relationships of Sucrose in Cookie and Cracker Systems. J. Sci. Food Agric. **63**, 133-176 (1993)

[8] L. Slade,H. Levine. Glass Transitions and Water-Food Structure Interactions. In Advances in Food and Nutrition Research, ed. J.E.Kinsella, San diego:Academic Press, San Diego **38**, 103-269 (1994)

[9] L. Slade,H. Levine. Thermal Analysis of Starch and Gelatin. DMA of frozen aqueous solutions. Proceedings 13th Annual Conference, North American Thermal Analysis Society, ed. A.R. McGhie, 9/23-26, Philadelphia, PA (1984)

[10] T.J. Maurice, L. Slade., C. Page, C. Sirett, Polysaccharide-water interaction: Thermal Behavior of Rice Starch. (ISOPOW III-1984). In Properties of water in foods, eds. Simatos,D., Multon,J.L. M. Nijhoff, Dordrecht 1985, p.211-27

[11] H. Levine, L. Slade, Recent advances in applications of thermal analysis to foods. a special issue of J. Thermal Analysis **47**(5):1175-1616 (1996)

[12] M.G. Cowie. Polymer: chemistry & physics of modern materials. Chapman & Hall, New York 1991, p. 248

[13] M.T. Kalichevsky, E.M. Jaroskiewicz, J.M.V. Blanshard. Glass transition of gluten 1: Gluten and gluten-sugar mixtures. J Biol. Macromol.**14**:257-266 (1992)

[14] L.E. Nielsen. Mechanical properties of polymers and composites. Volume 1. Marcel Dekker, New York 1974, p. 52-190

[15] P. B. McNulty, D.G.Flynn, Force-deformation and texture profile behavior of aqueous sugar glasses. J. Texture Studies **8**:417-431 (1977)

[16] M.T. Kalichevsky, J.M.V. Blanshard, P.F. Tokarczuk. Effect of water content and sugars on the glass transition of casein and sodium caseinate. Int. J. Food Sci. & Tech. **28**:139-151 (1993)

[17] G. Blond. Mechanical properties of frozen model solutions. J. Food Engineering **22**(1-4):253-269 (1994)

[18] M.T. Kalichevesky, E.M. Jaroskiewicz, J.M.V. Blanshard. Glass transition of gluten. 2: The effect of lipids and emulsifiers. J. Biol. Macromol. **14**:267-273 (1992)

[19] C.A. Angell, R.C. Stell, W. Sichina, Viscosity-temperature function for sorbitol from combined viscosity and differential scanning calorimetry studies. J. Phys. Chem. **86**:1540-1542 (1982)

[20] R.M. Hill, L.A. Dissado, The temperature dependence of relaxation process. J. Phys. C15,5171-5193 (1982)

[21]T. Soesanto, M.C. Williams, Volumetric interpretation of viscosity for concentrated and dilute sugar solutions. J. Phys. Chem. **85**:3338-3341 (1981)

[22]A. L. Ollett, P. Parker, The viscosity of supercooled fructose and its glass transition temperature. J. Texture Study **21**:355-362 (1990)

[23]M. Peleg, Mapping the stiffness-temperature-moisturerelationship of solid biomaterials at and around their glass transition. Rheol. Acta **32**:575-580 (1993)

[24]M. Peleg, A model of moisture-induced plasticization of crunchy snacks based on Fermi's distribution function. J. Sci. Food Agric. **64**:467-473 (1994)