Determination of Green-Bond Strength in Tacky Poly(vinyl alcohol) Hydrogels

Omri Ben-Zion,[1] Mark Karpasas,[2] Amos Nussinovitch[1]

[1]*Hebrew University of Jerusalem, Institute of Biochemistry, Food Science and Nutrition, Faculty of Agricultural, Food and Environmental Quality Sciences, P.O. Box 12, Rehovot 76100, Israel*
[2]*Institute for Applied Bioscience, Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva 84105, Israel*

Received 27 September 2001; accepted 28 May 2002

Abstract: Pressure-sensitive tack is the adhesive property related to bond formation. It is a key issue when formulating hydrogel poultices for transdermal delivery, dressings, and bioelectrodes. Quantitative tack gives an indication of the potential ease and success of application when gels are brought into contact with skin. The effects of different dwell times and constant pressures on bond formation between tacky poly(vinyl alcohol) (PVA) hydrogels and a skin model were explored in the current study; these were correlated with viscoelastic properties in order to elucidate structure–function relationships. A rolling tack test was performed using a novel apparatus capable of simultaneously controlling the pressure and dwell time in a hydrogel/skin-model-probe system. PVA gels were formed via the freeze–thaw technique using Ca^{2+} ions. Lower calcium availability in PVA gels resulted in longer dwell times required to complete bond formation, decreased creep compliance (at 0.01 s) and a decreased $G'_{(\omega = 40)}/G'_{(\omega = 0.01)}$ ratio, all three leading to a loss in tack strength. All tested gels were found to have pressure-sensitive tack. The results of this study support the applicability of a rheological methodology and a novel tack-testing procedure to quantify green-bond formation in pressure-sensitive-adhesive PVA hydrogels. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 87: 2130–2135, 2003

Key words: PVA hydrogels; tack; pressure-sensitive adhesives; bond formation; viscoelastic properties

INTRODUCTION

Poly(vinyl alcohol) (PVA) and other adhesive gels are outstanding choices for use in medical applications such as transdermal drug delivery,[1] bioelectrodes,[2] and dressings.[3] Pressure-sensitive tack (initial bond formation) is an essential property of such products. Insufficient tack may prevent attachment to the skin, whereas excessive tack may leave adhesive residue on removal or cause dermal irritation.

The factors controlling tack in many pressure-sensitive adhesive (PSA) materials have been previously explored.[4] However, not much is known about the mechanisms underlying tack in PVA gels adhered to skin. Urushizaki and coworkers[5,6] found a significant positive correlation between the rolling friction coefficient and dynamic moduli of PVA gels. Cha et al.[7] found the peel adhesion of cryogenic PVA hydrogels to be intimately tied to the state of Ca^{2+} ion hydration in an aqueous environment. They found that tack variations are affected by PVA concentration, molecular weight, number of freeze-thaw cycles, temperature of thawing, and gel thickness. Additional studies, utilizing PVA and other hydrocolloid gels, have been limited to mucoadhesion.[8] They explored tensile and peel adhesion mechanisms, but not tack.

Assorted empirical methods have been developed to understand how various factors influence pressure-sensitive tack.[9] They include the rolling ball, rotating drum, rolling cylinder, modified peel, and tensile probe tack tests. In practice, sticky PVA gels, as with many PSAs, have bond formation at very low pressure loads, a feature that is not detectable with most tack tests. Moreover, the possibility of studying extremely low dwell times is also restricted.

The objectives of this study were to determine the dwell time necessary for bond formation (green-bond) in tacky PVA hydrogels adhered to a skin model, using a modified rolling tack method and a previously proposed apparatus[10,11]; to study the effects of dwell time and constant pressure on the quantitative tack of the hydrogels; and to correlate the rolling tack with viscoelasticity in order to elucidate structure–function relationships.

MATERIALS AND METHODS

Testing apparatus

Figure 1 shows the assembly device; its parts are identified by number, listed in parentheses in the following description. An aluminum cylindrical probe roller (1) is mounted onto a balancing supportive frame (2)

Correspondence to: A. Nussinovitch.
Contract grant sponsors: Clore Foundation; Horowitz Foundation.

Journal of Applied Polymer Science, Vol. 87, 2130–2135 (2003)

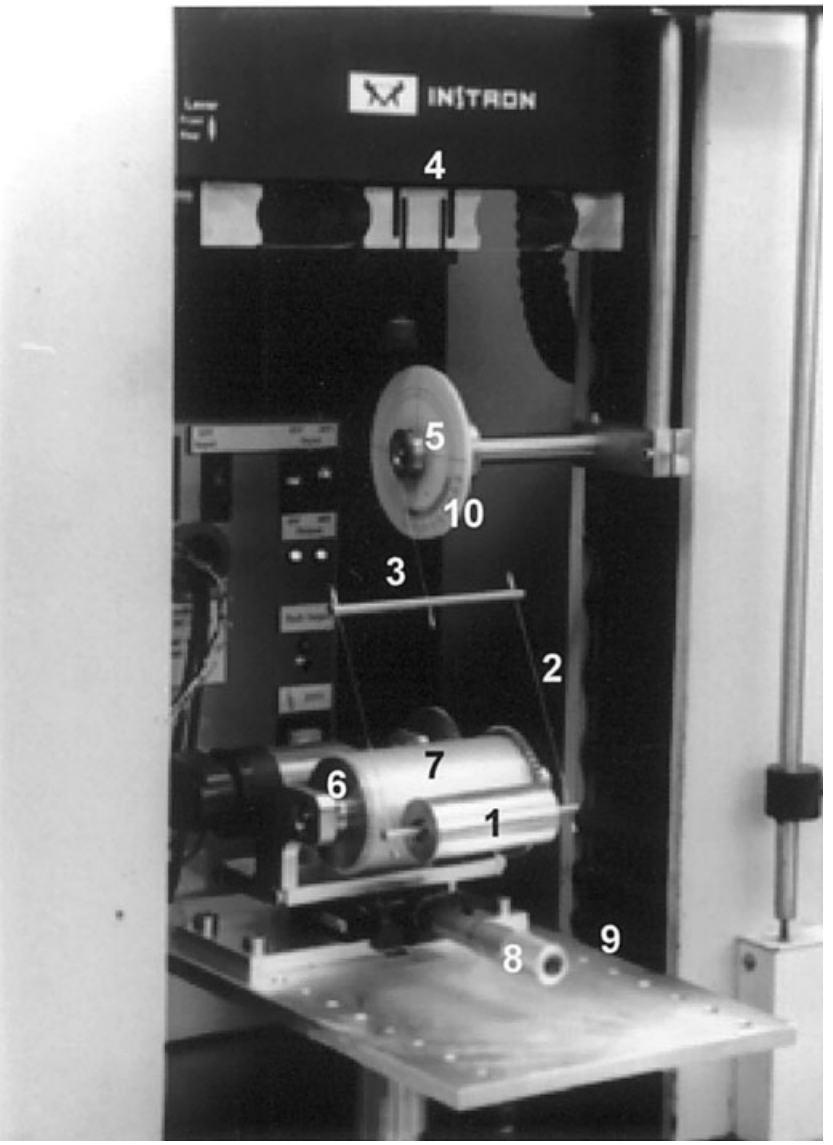

Figure 1 Instron Universal Testing Machine in conjunction with the rolling tack apparatus. Components: (1) cylindrical probe roller, (2) balancing supporting frame, (3) wire, (4) Instron UTM, (5) minipulley, (6) rotary drum, (7) molded gel, (8) linear micrometer positioning system, (9) incremental steps, (10) corrected protractor.

and hangs down via a centralized wire (3) to the crosshead of an Instron Universal Testing Machine (UTM) model 1011 (4), from Instron Company (Canton, MA). Underneath, a minipulley (5) is vertically centralized to the crosshead to maintain the uniaxial position of the hanging wire and the Instron UTM's LVDT (linear variable differential transformer). The probe roller assembly leans parallel to an aluminum rotary drum (6) covered with the gel sample being tested (7). The drum is propelled by a computerized motion-controlled DC motor. When the drum rotates, the probe roller, which is brought into contact with the test sample, spins freely and the Instron UTM's transducer records the adhesion force. The rotary drum is joined to a manual linear micrometer positioning system (8), which shifts by incremental steps (9) in response to selective movement toward the hanging probe roller. The rotary drum is shifted accordingly, allowing the angle of the hanging probe roller to be adjusted relative to the center of the Instron UTM's crosshead (the LVDT). An acting load down to 0.2 g/cm can be achieved by applying a simple trigonometric calculation, given an angle of 1.74×10^{-2} radians (1°) and a probe roller weight of 56 g. To maintain an accurate, fixed angle, a corrected protractor was designed (10), thereby eliminating deviations derived from the pulley diameter. Very low pressures can be achieved by employing very low angles.

Experimental design

PVA gel preparation

Aqueous deionized dispersions of PVA (18% w/v; MW: 124,000–186,000; degree of hydrolysis: 99.9%;

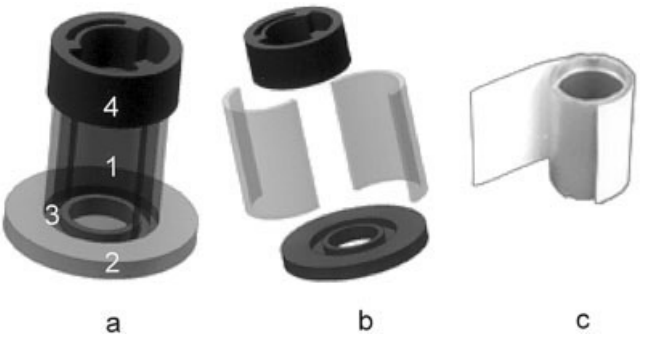

Figure 2 Tailor-made device for preparing cylindrical hydrogels: (a) assembled device, (b) disassembled device, (c) hydrogel-covered aluminum drum coated with PVC release film. 1, pair of hemicylinders; 2, base; 3, groove; 4, lid.

Aldrich, Milwaukee, WI) were heated to 100°C for 1 h, using a double-jacket vessel and a mixer (Heidolph Elektro GmbH & Co., Kelheim, Germany), and stirred with different concentrations of aqueous $CaCl_2$ solution [2%–14% (w/v) of the total mixture; Frutarom, Ltd., Haifa, Israel] for an additional 30 min. The mixed dispersions were cooled to 60°C before molding in a tailor-made device (described later) and then frozen at −20°C for 24 h, followed by 12 h of thawing at 25°C prior to testing.

Gel molding

A custom-made device for the production of gel-coated drum specimens was utilized [Fig. 2(a)]. A pair of Plexiglas hemicylinders (1) were mounted on a rigid base (2) by a compatible groove (3) and internally covered with rectangular-shaped, disposable poly(vinyl chloride) (PVC) release film/silicon-coated paper laminate (0.37 mm thick; Catalina Graphic Films Inc., Calabasas, CA). The latter was cut to precisely fit the joint cylinder's inner wall perimeter (160 ± 0.01 mm) using a digital paper guillotine (Schneider-Werk GmbH, Lubeck, Germany). Accordingly, the paper laminate formed a cylinder via its opposing perpendicular edges supporting each other by light pressure. An aluminum cylinder was concentrically positioned on the rigid base, leaving 2 mm of space between its outer wall and the PVC release film. A lid (4) was positioned on top of the assembly, with three deposition apertures above the space: two for gum-dispersion filling and one for air exclusion. After freezing, the lid and hemicylinders were disassembled [Fig. 2(b)], followed by removal of the gel-coated aluminum cylinder covered with the PVC release film [Fig. 2(c)]. Prior to testing, the PVC film was peeled off, resulting in a uniformly seamless gel-coated tube. The latter served as a rotating drum after being fixed to the rolling tack apparatus (Fig. 1, components 6 and 7). The probe roller was covered with a disposable artificial skin model (10% moisture), described elsewhere.[12]

Rolling tack testing procedure

Measurements were conducted at a sequence of 11 velocities (within the range of 0.02–1.88 m/s, 8 s/velocity) and under 5 pressures, presented as longitudinal load, that is, load per unit length (within the range of 0.2–6 g/cm by employing angles of 1° to 33°, respectively, using a 56-g probe). Tack results for each velocity–pressure combination were calculated as the average of three determinations, expressed as force per unit width. New specimens were used for each measurement. All tests were conducted at room temperature at ~60% relative humidity (RH).

Dynamic rheological measurements

The viscoelastic properties of the PVA hydrogels were tested with a constant stress rheometer (Carri-Med CSL-50, Surrey, UK) using parallel plates at 5% deformation. Tests were conducted in the linear viscoelastic range. Storage modulus (G'), loss modulus (G''), tangent δ (G''/G'), and complex viscosity [$\eta^* = (G'^2 + G''^2)^{1/2}/\omega$ were recorded in a frequency (ω) range of 0.01–40 Hz (applied stress of 50 Pa). Instantaneous creep compliance (J_0) was recorded after 0.01 s of an applied constant stress of 350 Pa, utilizing high-speed sampling (190 points per first second). All tests were conducted at room temperature at ~60% RH.

RESULTS AND DISCUSSION

Figure 3 shows the average calculated tack values for each testing time interval versus velocity for a PVA gel subjected to a longitudinal load of 1.6 g/cm. All curves went through a maximal point and then declined to a final measured tack of 0. In a velocity range

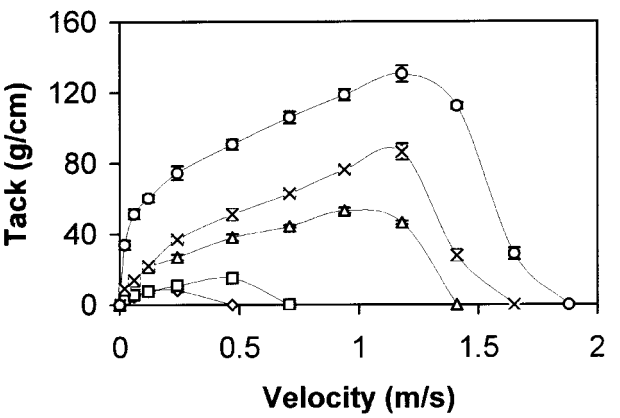

Figure 3 Tack versus rolling velocity for PVA gels with various Ca concentrations—◇: 2; □: 5; △: 8; ×: 11; ○: 14% (w/v) Ca; each tack value is the average of three determinations ± SE; longitudinal load: 1.6 g/cm.

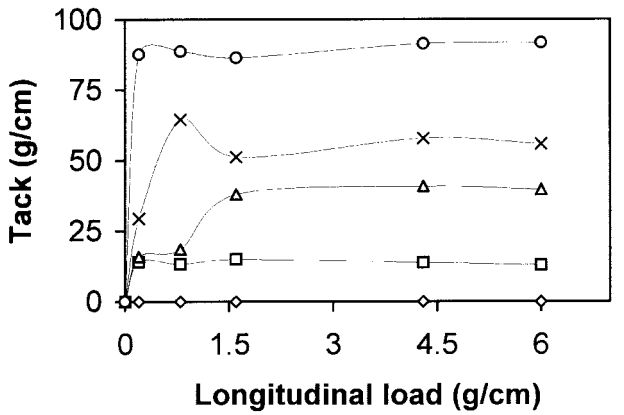

Figure 4 Rolling tack versus longitudinal load for PVA gels with various Ca concentrations—◇: 2; □: 5; △: 8; ×: 11; ○: 14% (w/v) Ca; each tack value is the average of three determinations ± SE; velocity: 0.47 m/s.

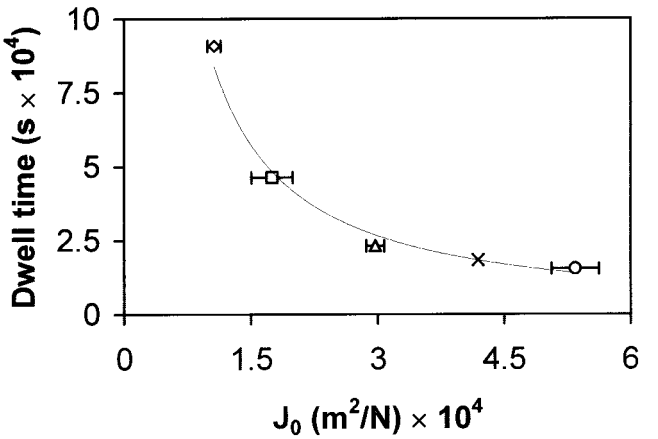

Figure 5 Approximated dwell time versus creep compliance, $J_{0(0.01)}$, for PVA gels—◇: 2; □: 5; △: 8; ×: 11; ○: 14% (w/v) Ca. Longitudinal load: 1.6 g/cm.

of 0.24–1.18 m/s, maximal tack values of 8.2 ± 0.8, 15 ± 0.7, 53.17 ± 1.5, 86.4 ± 4.6, and 130.6 ± 4.7 g/cm were observed for gels with Ca concentrations of 2%, 5%, 8%, 11%, and 14% (w/v), respectively. The typical shape of the curves is an outcome of the simultaneously occurring bonding and debonding processes. At any given velocity, enhanced adhesion theoretically corresponds to a higher dissipation energy at debonding, resulting in a higher measured tack value.[13] For any PVA gel, after reaching its peak value, debonding occurs before efficient contact with the skin model is realized, and the measured tack force tends to decrease. Thus, a transition of tack values from ascending to descending corresponds to loss of tack. Higher Ca concentrations shifted the curves' maximal tack values toward higher velocities. The velocity at which such a transition occurs can be associated with the critical dwell time (defined as the duration of contact between the gel and the probe) required to complete bond formation.

For all PVA gels, rolling tack values were found to increase to an asymptotic value with increasing longitudinal loads (Fig. 4). Higher probe contact pressures enhanced surface wetting and mechanical interlocking,[14] leading to bond formation.

Figure 5 shows the relationships between the critical estimated dwell times and creep compliance (J_0) at 0.01 s for the various PVA gels tested. To estimate dwell time, the gel/skin-model contact area was approximated, assuming the gel to be almost nondeformable within the range of the tested pressure loads. A rough estimate of 0.017 rad (= 1°, equivalent to 2.18 × 10^{-2} cm, for a given probe roller 2.5 cm in diameter) was made for the maximal width dimension affected by the longitudinal contact area, as demonstrated in Figure 6. This was in agreement with the visible contact surface area between the probe roller and the gel-coated drum. Accordingly, velocities of 0.24–1.41 m/s corresponded to dwell times of 9.1–1.55 × 10^{-4} s, respectively. It is worth noting that in practice, dwell times at elevated velocities may be slightly shorter than estimated values. When velocity increased, the gel plane supported the probe roller at smaller deformations[15] (a result of elastic stress); thus, the contact area decreased in parallel to dwell time. This behavior is typically nonlinear. Creep compliance was found to be strongly associated with adhesive bond formation. As the $J_{0(0.01)}$ of the gel increased (higher Ca concentration), a shorter dwell time was sufficient to effect bond formation. Increased gel compliance was assumed to improve wetting and mechanical interlocking, thus compensating for tack loss at short contact durations with the skin-model probe.

Figure 7 shows the relationships between the rolling tack values (longitudinal load = 1.6 g/cm; velocity = 0.71 m/s) and the $G'_{(\omega = 40)}/G'_{(\omega = 0.01)}$ ratio for the five tested PVA gels. G' values at such low and high frequencies are known to correlate with bonding and debonding time intervals, respectively.[16] Higher $G'_{(\omega = 40)}$ and lower $G'_{(\omega = 0.01)}$ result in a higher ratio, which is associated with increased tack. The high lin-

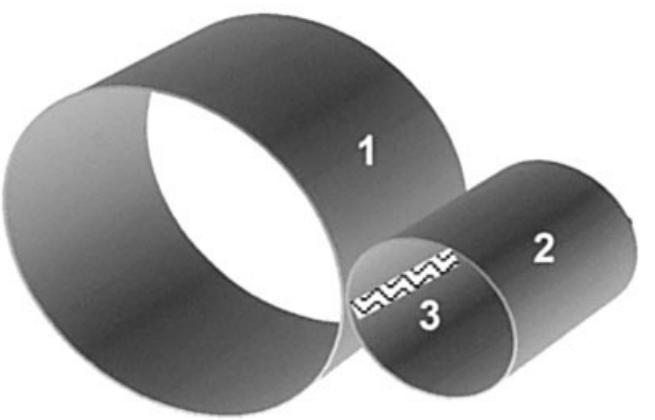

Figure 6 (1) Hydrogel-coated rotary drum; (2) probe roller; (3) contact area.

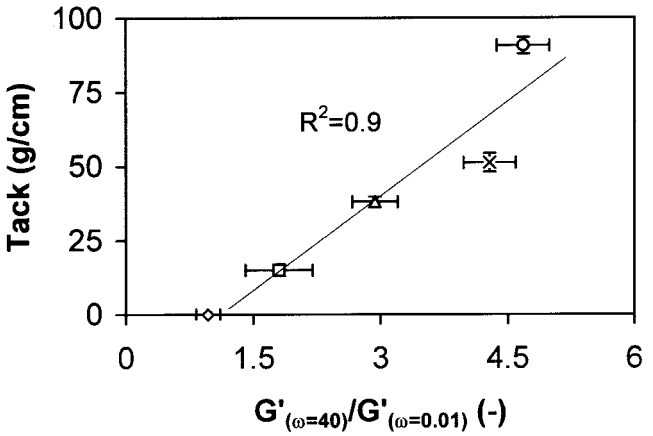

Figure 7 Rolling tack versus $G'_{(\omega = 40)}/G'_{(\omega = 0.01)}$ for PVA gels—◇: 2; □: 5; △: 8; ×: 11; ○: 14% (w/v) Ca. Longitudinal load: 1.6 g/cm; velocity 0.47 m/s.

ear correlation ($r^2 = 0.90$) is an indication of the ability to achieve the requested tack in PVA gels. This was supported by the findings of decreased G' and η^* (decreased elasticity) or increased G'' and tangent δ with increased Ca concentration at various frequencies [Fig. 8]. This observation was not surprising, given that during bonding of a PSA, it must exhibit sufficient viscous flow when the rate of deformation is low to conform to the adhered surface.[17]

In general, the relationships between viscoelastic properties and tack in PVA gels (Figs. 5 and 7) can be explained by the mechanism of gelation. Successive freeze-and-thaw cycles of aqueous PVA solutions result in a three-dimensional network held together by crystallites acting as physical crosslinks,[18,19] mostly as a result of hydrogen bonding between PVA molecules.[20] Free-polymer molecular chains contribute to tackiness, whereas entangled chains provide cohesiveness. The degree of crystallinity can by manipulated by the weight percent of PVA, freeze-and-thaw times or temperatures, number of freeze-and-thaw cycles, and degree of molecular hydrolysis,[19] or, as shown in this and other works,[7] by the addition of divalent metallic salts such as Ca. These ions do not support strong complex bonds with the PVA molecular chains because of their high state of hydration.[7] The dissolution of highly concentrated $CaCl_2$ (up to 14% w/v) in the water component of the formulation increased the osmotic pressure, which decreased freezing. Consequently, the opportunity for crystallite formation was reduced, and, in turn, the existence of free polymer chains prevailed, leading to improved tack. Figure 9 illustrates a possible PVA hydrogel molecular structure after the freeze–thaw process.

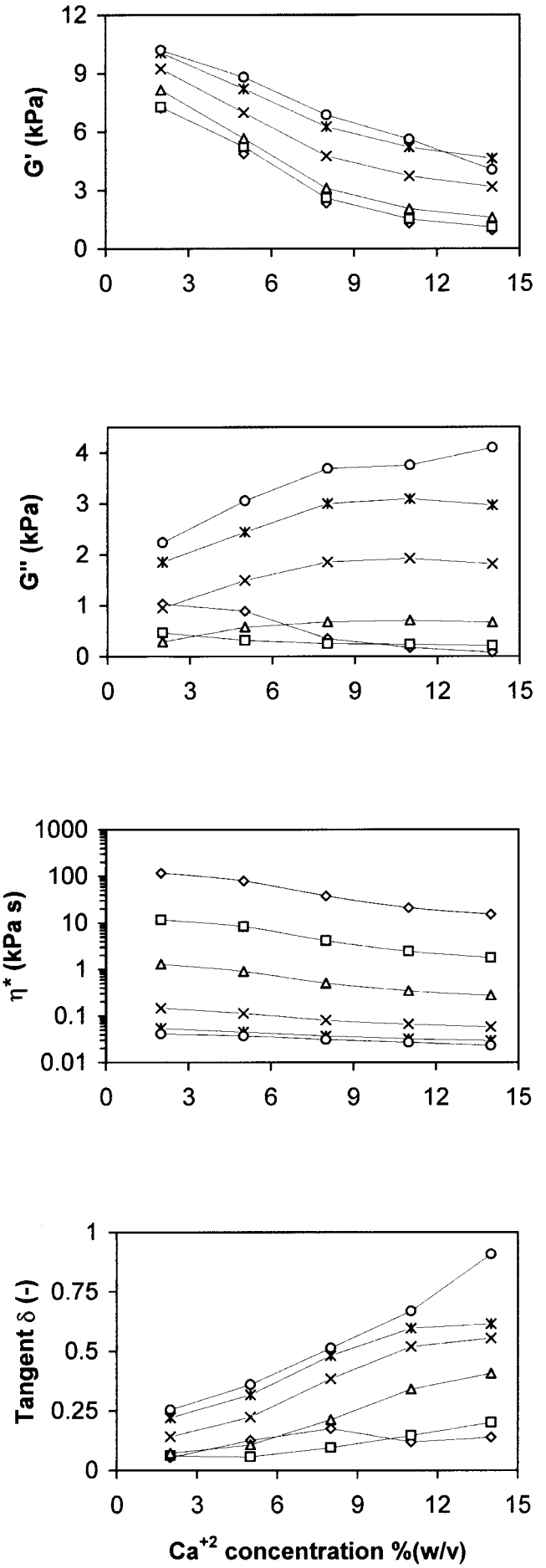

Figure 8 Dynamic rheological parameters (G', G'', tangent δ, and η^*) for PVA gels with various Ca concentrations tested at various frequencies (◇: 0.01; □: 0.1; △: 1; ×: 10; ✳: 30; ○: 40 Hz).

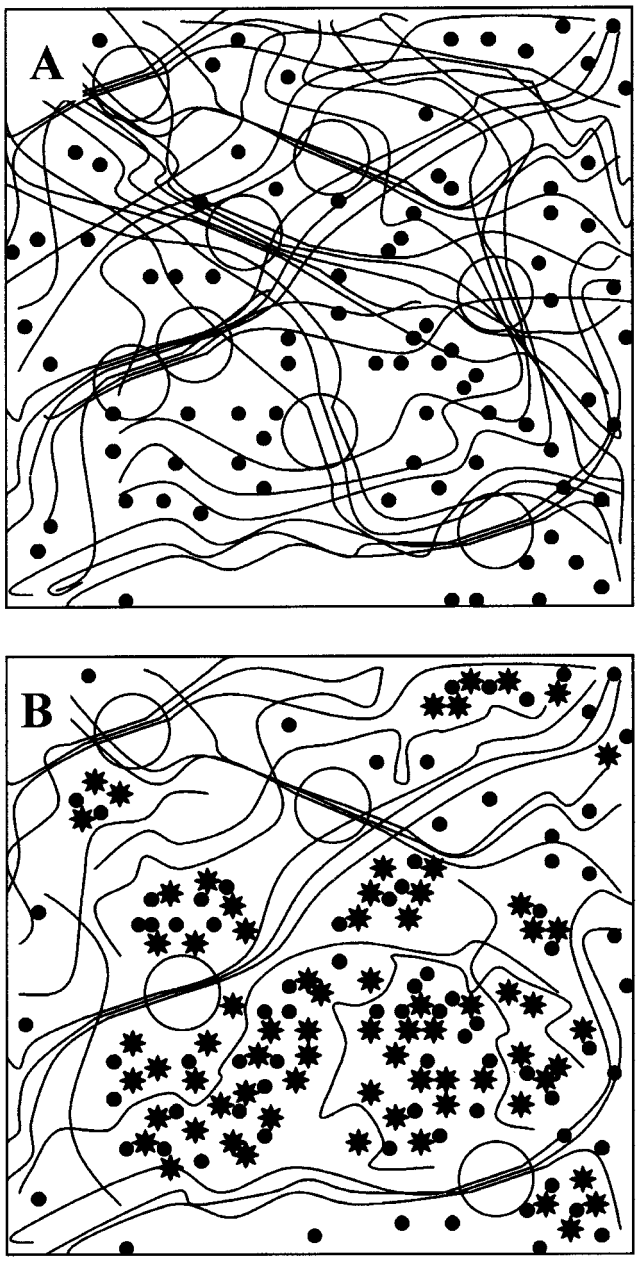

Figure 9 Schematic representation of a possible PVA/$CaCl_2$ hydrogel molecular structure after freezing-thawing process. Circled areas are crystallites; ●: water; ★: Ca^{+2}; (A) gel with no Ca added; (B) gel with high Ca content.

PVA–Ca hydrogels consisting of high-molecular-mass polymers (124,000–186,000 Da) and prepared by the method described above provided a cohesive bond (did not leave adhesive residue on removal), as opposed to PVA gels with lower molecular masses (89,000–98,000 and 85,000–146,000 Da), prepared with the same polymer and $CaCl_2$ concentrations. The latter observation and the fact that tacky PVA hydrogels are essentially nontoxic and do not contain any leachable impurities[18] support the potential use of these hydrogels in medical applications, such as transdermal drug delivery systems.

CONCLUSIONS

Our novel, unique rolling tack tester (patent pending) was able to simultaneously control the pressure sensitivity and dwell time of a PVA hydrogel. Analysis of tack versus probe-roller velocity offers an outstanding tool for studying mechanisms and times related to the stages in the bonding and debonding processes. The strong observed relationships between PVA gel viscoelasticities and rolling tack values offer a possible explanation for structure–function links. This novel apparatus and testing methodology can be used for any formulated hydrocolloid tacky gel. This type of testing may also be appropriate for quality-control measurements of ready-to-use transdermal delivery systems, bioelectrodes, and the like.

The authors thank the Department of Instrumental Design at the Weizmann Institute of Science in Rehovot, Israel, especially B. Pasmantirer, J. Ankaoua, and A. Einhorn, who helped us design and construct the tack apparatus. The photographic expertise of O. Tevel is most appreciated.

References

1. Sugibayashi, K.; Morimoto, Y. J Controlled Release 1994, 29, 177–185.
2. Keusch, P.; Essmyer, J. L. U.S. Pat. 4,684,558 (1987).
3. Romaine, J. W. U.S. Pat. 4,377,160 (1983).
4. Hammond, F. H. In Handbook of Pressure-Sensitive Adhesive Technology; Satas, D., Ed.; Van Nostrand Reinhold: New York, 1982; pp 32–49.
5. Urushizaki, F.; Mizumachi, H. Chem Pharm Bull 1991, 39, 159.
6. Urushizaki, F.; Yamaguchi, H.; Mizumachi, H. Yakugaku Zasshi 1986, 106, 491.
7. Cha, C. W.; Hyon, S. H.; Graiver, D.; Ikada, Y. J Appl Polym Sci 1993, 47, 339.
8. Peppas, N. A.; Sahlin, J. J. Biomaterials 1996, 17, 1553.
9. Johnston, J. Proc Pressure-Sensitive Tape Council Technical Seminar 1983, 126–146.
10. Ben-Zion, O.; Nussinovitch, A. J Adhes Sci Technol 2002, 16, 227.
11. Ben-Zion, O.; Nussinovitch, A. U.S. Pat. Appl. (2002).
12. Ben-Zion, O.; Nussinovitch, A. Food Hydrocolloids 1997, 11, 429.
13. Zosel, A. Adhesives Age 1989, 32, 42.
14. Hamed, G. R.; Shieh, C. H. J Appl Polym Sci 1983, 21, 1415.
15. Poschel, T.; Schwager, T.; Brilliantov, N. V. Eur Phys J B 1999, 10, 169–174.
16. Chu, S. G. In Adhesive Bonding; Lee, L. H., Ed.; Plenum Press: New York, 1991; pp 97–138.
17. Wood, T. G. Adhesives Age 1987, 30, 19.
18. Mongia, N. K.; Anseth, K. S.; Peppas, N. A. J Biomater Sci Polymer Edn 1996, 7, 1055–1064.
19. Peppas, N. A.; Stauffer, S. R. J Controlled Release 1991, 16, 305–310.
20. Nagura, M.; Hamano, T.; Ishikawa, H. Polymer 1989, 30, 762–765.