Rheology of Poly(*N*-vinyl pyrrolidone)–Poly(ethylene glycol) Adhesive Blends under Shear Flow

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ABSTRACT: The rheological properties of adhesive miscible blends of high-molecular-weight poly(*N*-vinyl pyrrolidone) (PVP) with short-chain poly(ethylene glycol) (PEG) under oscillatory and steady-state shear flow have been examined with dynamic mechanical and squeezing-flow analysis. The latter allows the rheological characterization of adhesive blends under conditions modeling adhesive-bond formation as a fixed compressive force is applied to an adhesive film. The most adhesive PVP blend with 36 wt % PEG has been established to flow like a viscoplastic (yield stress) liquid with a power-law index of about 0.12. The study of the apparent yield stress as a function of the PVP–PEG composition, content of sorbed water, molecular weight of PVP, and temperature shows that the occurrence of a yield stress in the blends results most likely from a noncovalent crosslinking of PVP macromolecules through short PEG chains by means of hydrogen bonding of both terminal OH groups of PEG to the complementary functional groups in PVP monomer units. A molecular mechanism of PVP–PEG interaction was established earlier by direct and independent methods. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 522–537, 2006

Key words: adhesives; blends; rheology; water-soluble polymers

INTRODUCTION

Typical pressure-sensitive adhesives (PSAs) represent a special class of soft elastomers that couple rubberlike elasticity with very dissipative properties.[1–4] A low elastic modulus is necessary to provide tack, which is defined as the capability of a material to form a strong adhesive bond with an adherend by the application of a very slight pressure during a short contact time (usually 1–2 s).[5,6] The molecular mechanism underlying the tack involves the easy deformation of the adhesive to establish a molecular contact with the adherend.[5] However, having good tack is a necessary but insufficient condition for pressure-sensitive adhesion. To be considered a PSA, a tacky material should also resist creep at moderate levels of stress. Crosslinked, entangled, or structured elastomers provide the necessary chemical structure to dissipate energy upon debonding.

Pressure-sensitive adhesion is traditionally treated as a specific property of a material. This property can be adequately described by Dahlquist's criterion of tack, which has established that various PSAs possess a shear modulus (*G*) below 0.1 MPa.[3] The physical significance of this criterion at a molecular level is that the elasticity modulus is a measure of the ratio between the values of the stress (which characterizes the cohesion energy) and deformation (which has been established to be mainly controlled by the molecular weight and free volume of the adhesive material).[7] Until recently, Dahlquist's criterion of tack described fairly reasonably the interrelationship between the adhesive and rheological properties of all the PSAs known to date. However, very recently a new class of hydrophilic PSAs has been obtained, exemplified by poly(*N*-vinyl pyrrolidone) (PVP)–poly(ethylene glycol) (PEG) miscible blends,[8,9] whose behavior appreciably disobeys Dahlquist's criterion. A comparison of the tack properties of the PVP–PEG adhesives and their linear viscoelastic properties showed a very strong decoupling between the small-strain and large-strain properties of the adhesive indicative of a pronounced deviation from rubber elasticity.[7] As a result, it is impossible to predict even qualitatively the large-strain and adhesive properties of hydrophilic PVP–PEG blends from dynamic mechanical data, which are

related to the linear elastic behavior of the blends at small strains.[7,9] In particular, it has been shown that Dahlquist's criterion holds for PVP–PEG systems in the area of large strain and in the vicinity of fracture rather than in the linear elastic region of deformation. The implication of this fact is that the structure of a PVP–PEG adhesive under an applied tensile stress is modified in such a way that the behavior typical of PSAs is a result of large deformations. In turn, this means that the interpretation of the phenomenon of pressure-sensitive adhesion solely as a property of the intact (equilibrium) structure of a material is not always adequate and that to gain further insight into this phenomenon, the adhesion should also be treated as a process involving a change in the structure and properties of the material with time under applied stress.

Indeed, the term *property* is often perceived as a feature of a specific molecular structure existing at equilibrium. Reducing the concept of adhesion to an equilibrium (undistorted) state of material would be a gross simplification because adhesion (or more specifically the rupture of an adhesive bond) is a phenomenon that causes a series of transformations of the structure of the adhesive material under the applied bonding and detaching stress. The order and arrangement in time of these structural transformations have great importance for the perception of the phenomenon as a whole.

The process of pressure-sensitive adhesion can be regarded as three-stage. Adhesive bonding under a compressive force (I) is followed by the removal of the bonding pressure and the relaxation of the adhesive material (II), after which the application of the tensile stress brings the process to an end when the fracture of the adhesive joint occurs (III) via adhesive or cohesive mechanisms. The subject of this article is a rheological description of the behavior of a PVP–PEG hydrophilic adhesive under conditions modeling the first stage of the adhesion process: adhesive bonding. With this purpose in mind, the rheological behavior of the PVP–PEG adhesive under a fixed compressive force is analyzed as a function of time in terms of the shear stress, shear strain, shear rate, and viscosity.

From the point of view of their rheological and adhesive properties, hydrophilic systems such as PVP–PEG blends are considerably more complex than typical PSAs, which are hydrophobic.[4] The hydrophilic polymers often display reversible specific interactions that can significantly alter the rheological properties.[10,11] These reversible interactions can be not only hydrophobic[12,13] but also much stronger electrostatic[14] or hydrogen bonds.[15] They typically introduce another timescale and a pronounced nonlinearity in the deformation properties because a deformation to large strains can destroy a nonpermanent network of interactions that may not be able to reform instanta-

neously. These aspects have been treated in theoretical[10,11] and experimental publications.[16] We have contributed to this topic by studying the rheological properties of a specific type of hydrophilic polymeric blend, which is suitable for PSA applications.

Our model system is an adhesive blend of high-molecular-weight PVP with a low-molecular-weight PEG. The adhesive[8,9] and tensile properties[7] of the PVP–PEG blends have been the focus of extensive work, which has been complemented by studies focusing on more molecular spectroscopic techniques.[17,18] As a result, much is known about the compositions, which provide optimum adhesive properties, and the organization of the polymer chains in the blends.[19] The main results from these studies can be summarized as follows.

Pressure-sensitive adhesion appears in the PVP–PEG blends within a very narrow range of compositions that is very affected by the amount of sorbed water.[8,9] In essence, only blends containing 31–41 wt % PEG-400 and 4–12% absorbed water display PSA properties, whereas both parent polymers and dry blends possess no adhesion.

Spectroscopic investigations have shown that hydrated PVP–PEG forms a complex network of nonpermanent hydrogen bonds between terminal PEG hydroxyls and carbonyl groups in the PVP monomer units.[17,18] Because the PEG chains bear two terminal hydroxyl groups, they act as hydrogen-bonding, labile, and transient crosslinkers between the longer PVP macromolecules. Although every monomer unit in the PVP macromolecule contains one reactive carbonyl group, only nearly 20% of them can be crosslinked by the shorter chains of PEG-400 in a network of hydrogen-bonded complexes within a wide range of PVP–PEG compositions. This behavior characterizes the PVP–PEG hydrogen-bonded complex as exhibiting a nonequimolar stoichiometry and a network supramolecular structure.[19]

The observed decoupling between small-strain and large-strain behavior of the PVP–PEG blends has been attributed to the existence of two types of networks.[7] The first network is provided by the physical entanglements of longer PVP chains and contributes mainly to the material behavior under small deformations. The second network is associated with much shorter and flexible chains of PEG and is formed by hydrogen bonding.

Although the mechanism of deformation under uniaxial extension of the PVP–PEG adhesive has been extensively investigated, much less is known about its deformation behavior in shear at larger strains, which is essential for a more thorough insight into the phenomenon of tack. In this work, we investigate the rheological properties of PVP–PEG adhesive blends by comparing the standard dynamic, small-strain oscillatory shear with a relatively simple method seek-

ing to reproduce the contact formation under stress, namely, the squeezing-flow geometry used typically for liquids under a fixed compressive force. Although a quantitative analysis of this method is not straightforward,[20] particularly for such complex soft materials, it tests the PVP–PEG adhesive in the large-strain region and does provide some very useful insights into the behavior of the adhesive blends during bond formation, outlining qualitatively the rheological mechanisms that underlie the pressure sensitivity of viscoelastic adhesives.

EXPERIMENTAL

Sample preparation

PVP (Kollidon K-17 and K-90; weight-average molecular weight = 2000–8000 and 1,000,000 g/mol, respectively; BASF, Ludwigshafen, Germany) and PEG (molecular weight = 400 g/mol; Carbowax Sentry NF, Union Carbide Corp., Danbury, CT) were used as received. Both polymers were hygroscopic, and the degree of their hydration, evaluated by the weight loss under drying at 105°C, was taken into account to prepare physical blends containing 20–41 wt % PEG-400. Depending on the relative humidity (RH) of the surrounding atmosphere, the PVP degree of hydration ranged from 6 to 8 wt %, whereas PEG contained less sorbed water (0–1 wt %).

To prepare the samples for dynamic mechanical analysis (DMA) measurements, the PVP–PEG solutions in ethanol were poured into Teflon molds (2 cm deep) and were left at room temperature for 7 days to evaporate most of the solvent. The resulting films (1–1.5 mm thick) were then dried 3 h *in vacuo* at 65°C. The water content of the adhesive films was then equilibrated by the samples being left at room temperature in desiccators under constant levels of RH (53 and 100%) for 6 days and overnight, respectively. The required RH level of 53% was provided by a sulfuric acid solution with a density of 1.29 g/cm^3. After the samples were conditioned and before testing, the water content was measured for a selected sample by weight loss after thorough drying *in vacuo* at 90°C. Although the sample upon drying contained about 1 wt % water, for conditioned samples the films contained 11 and 40 wt % water, respectively.

For the squeezing-flow analysis, the films of PVP–PEG blends were prepared by the dissolution of PVP and PEG in a common solvent (ethyl alcohol or water), the casting of the solution onto the siliconized surface of a poly(ethylene terephthalate) PEBAX-600 release liner (60 μm thick), and finally the evaporation of the solvent at the ambient temperature and RH for 3 days until a constant weight was attained. In the casting solution, the concentration of PVP in ethyl alcohol was about 40 wt %. The solvent removal was verified by

Fourier transform infrared (FTIR) spectroscopy; we observed a lack of methylene group stretching vibrations at 2974 and 1378 cm^{-1} in the IR spectrum. The hydration of freshly prepared PVP–PEG blends containing 36 wt % PEG-400 averaged to 6.5 ± 0.8 wt %. From this point on, the term *hydrogel* is used to designate equilibrium hydrated PVP–PEG blends.

DMA

The dynamic mechanical properties of the PVP–PEG adhesives in the linear viscoelastic regime were measured on an RDA II parallel-plate rheometer from Rheometrics (Piscataway, NJ). Pellets (8 mm in diameter) were taken out of these films with a circular punch. At room temperature, each sample was positioned in the rheometer and kept for 15 min under a slight pressure to ensure good adhesion between the polymer blend and the rheometer plates. The temperature was then gradually decreased to the lowest temperature of the experiment.

For the blends containing 31 or 36 wt % PEG, we varied the temperature from −20 to 130°C, in 5°C steps from −20 to 80°C and in 10°C steps from 90 to 130°C. The frequencies varied from 0.05 to 100 rad/s (10 points per decade) for each temperature below 25°C and from 0.05 to 500 rad/s for higher temperatures. For the blend containing 41 wt % PEG, we varied the temperature from −50 to 0°C in 5°C steps, and the frequencies were varied from 0.05 to 100 rad/s (10 points per decade). The amplitude of deformation was chosen to be in the linear region over the whole range of temperatures. For our PVP–PEG blends, this zone corresponds to a deformation varying from 0.1 to 1%, depending on the temperature.

Finally, master curves as a function of frequency were constructed by the application of the time–temperature superposition (TTS) principle. For the 31 and 36% PEG samples, a reference temperature of 20°C was chosen, whereas for the 41% blend, the highest temperature at which the measurement was possible, 0°C, was chosen as a reference temperature.

Squeeze–recoil analysis

The viscoelastic properties of the PVP–PEG adhesives under a squeezing flow were measured on a parallel-plate high-precision dilatometer based on a DTMD thermomechanical analyzer (Scientific and Technological Center of Unique Instrumentation, Russian Academy of Science, Moscow, Russia) described by Kotomin and Kulichikhin.[21] A hydrogel sample 0.5–1.5 mm thick had initially the same size as an upper cylindrical quartz rod 6 mm in diameter with a flat end. Over the course of the test, the sample was compressed between a bottom immovable plate and the upper cylindrical rod. At the beginning of the test, a fixed

total force, F, was applied to the upper rod by means of weights of 1–500 g, and the rod displacement {gap between the plates [$h(t)$] was measured with an accuracy of 1 μm as a function of time. As the compression proceeded, the material was extruded from a gap between the upper and bottom plates, and the total compression area remained constant and equal to the cross section of the upper rod.

Although h decreased under a fixed compressive force, the average shear rate and the average stress in the gap decreased continuously. As the shear stress at the edges of the contact tended toward the yield stress of the sample, the rod ceased to move, and the gap between the plates remained constant. This limiting value of the gap (h_∞) was used for a direct evaluation of the apparent yield stress (τ_y). When the stress provided by the compressive force became comparable to the value of the yield stress of the adhesive, the contribution of the flow process to the force became negligible, and an apparent yield stress could then be calculated from the value of h_∞ by eq. (1):[21]

$$\tau_y = \frac{2h_\infty F}{\pi R^3} \tag{1}$$

where τ_R is the yield stress and R is the radius. The dependence of this yield stress on the temperature was estimated by the heating of the samples at a slow rate of 0.5°C/min from the ambient temperature up to 200°C.

Because the shear field between the two parallel plates was not uniform, the yield stress value could be evaluated only for the edge area of the operating unit. This apparent value of the yield stress has been reported to differ from the true yield stress of a material by a factor of 2/3.[22] To compare the apparent yield stress measured with the squeezing-flow technique with the true value established with a constant shear stress rheometer, a specific test was carried out with a shear plastometer with parallel plates. The bottom plate was fixed, and the upper plate moved under the action of a constant force. In our case, the plates had dimensions of 2.5 × 4.0 cm² and a rough contact surface. The sample thickness in the gap was 0.5 mm. The minimum value of shear stress causing plastic deformation of the sample under consideration was accepted as a value of the true yield stress.

RESULTS AND DISCUSSION

Viscoelastic properties of a PVP–PEG blend under oscillatory shear

Before proceeding to the rheological characterization of the behavior of the PVP–PEG adhesive under a compressive force as a function of time (process), let us consider first the linear elastic properties of the material under conditions in which the structure does not change. These experiments were performed in a parallel-plate rheometer, and the amplitude of deformation was chosen to be in the linear region over the whole range of temperatures. For our PVP–PEG blends, this zone corresponds to a deformation varying from 0.1 to 1%, depending on the temperature.

These experiments provide information at different levels. First of all, TTS can be attempted with the curves obtained at different temperatures. A successful TTS is an indication of a uniform temperature dependence for all relaxation times of the material and typically is a good indication of the absence of two independent phases. In our case, the PVP–PEG blends show the occurrence of two relaxation transitions, even though their phase behavior is rather typical of single-phase systems.[19]

The second type of information is contained in the functional dependence of the frequency shift with temperature. Generally, in the vicinity of the glass-transition temperature (T_g), at which the free volume is nearly constant for a great number of polymers, and at $T < (T_g + 100)$ (where T is the temperature), the temperature dependence of the shift factor, a_T, is defined by the well-known Williams–Landel–Ferry (WLF) equation:[23]

$$\log a_T = \log \frac{\omega}{\omega_R} = -\frac{C_1^0(T - T_R)}{C_2^0 + (T - T_R)} \tag{2}$$

where ω is the frequency, ω_R and T_R are the reference frequency and temperature, respectively, and C_1^0 and C_2^0 are constants.

According to the results of the peel and probe tack test measurements,[8,9] a blend of high-molecular-weight PVP with liquid short-chain PEG-400 (36 wt %) exhibits the best adhesion. Figure 1 plots the logarithm of the frequency shift for this blend against the temperature shift, $T–T_R$. Because the reference temperature in this work has been chosen to be 273 K (0°C), Figure 1 illustrates the temperature dependence of a_T. As follows from the data in Figure 1, the WLF equation [eq. (2)] describes fairly reasonably the experimental data.

Figure 2 compares the temperature dependence of the shift factors for PVP blends with different amounts of PEG-400. At low temperatures, the shape of the log a_T–T curves is practically unaffected by the PEG content, but at temperatures above 15–20°C, the increase in the PEG content results in smaller frequency shifts at equivalent values of the temperature difference. For all the blends examined, the WLF equation [eq. (2)] provided a reasonable fit of the experimental data, but the higher the PEG content was, the lower the fitted values were of the C_1^0 and C_2^0 constants (Table I). This finding is quite explainable because the physical sig-
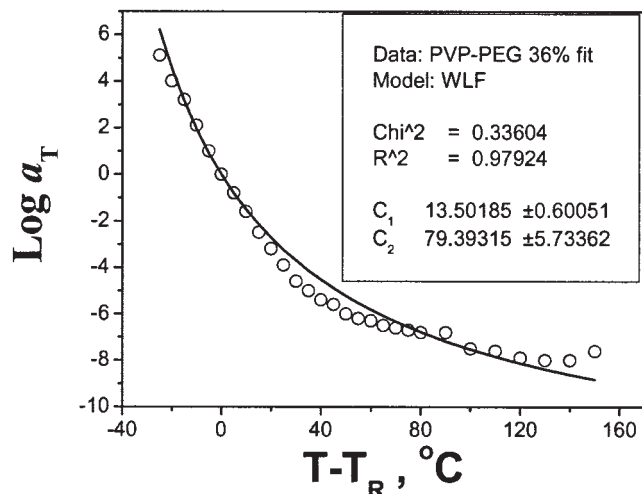
Figure 1 Relationship between the frequency shift and temperature shift for PVP blends with 36 wt % PEG-400. The points designate measured data. The curve represents the relationship predicted with the WLF equation [eq. (2)].

nificance of the C_1 constant in the WLF equation and the product of C_1C_2 goes back to the reciprocal of the free volume fraction and to the thermal expansion coefficient at the glass transition, respectively.[23] This is consistent with the recently found results of Li et al.[24] with positron annihilation spectroscopy: there is only a single population of free volume in the PVP–PEG blends, and the amount of free volume increases with the PEG-400 content. PEG is a good plasticizer of PVP.[19] As demonstrated by Bairamov et al.,[25] oligomeric PEG fractions are good solvents for PVP. It is well recognized that plasticizers and solvents increase the free volume in polymers.

In Figure 3, the temperature dependence of the shift factor for the PVP blend with 36% PEG is presented in terms of the Arrhenius equation:
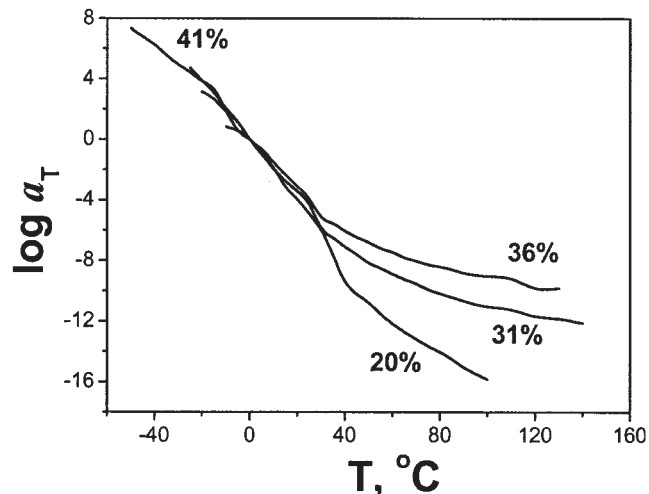
TABLE I
Values of the C_1^0 and C_2^0 Constants in the WLF Equation [eq. (2)] for PVP–PEG Blends at a Reference Temperature of 0°C

PVP–PEG	C_1^0	C_2^0	R^2
20% PEG	54.13 ± 8.29	261.46 ± 51.45	0.99
31% PEG	17.41 ± 0.90	84.69 ± 7.86	0.98
36% PEG	13.50 ± 0.60	79.39 ± 5.73	0.98

$$\ln \frac{\varpi}{\varpi_R} = -\frac{\Delta H}{R}\left[\frac{1}{T} - \frac{1}{T_R}\right] \tag{3}$$

where ΔH is a temperature coefficient that is related to the activation energy of the relevant process and ϖ and ϖ_R are the current and reference frequencies, respectively. As is obvious from Figure 3, the Arrhenius plot exhibits two linear regions, with a transition point at 18°C corresponding to the point of cleavage (divergence) of the log a_T–T curves presented in Figure 2. Similarly, two-branch Arrhenius plots are also typical for other PVP–PEG blends studied, indicating different values of the activation energy of relaxation processes occurring at higher and lower frequencies (temperatures) and a transformation of the material structure that underlies this change in the activation energy.

DMA provides a very accurate method of determining the storage modulus (G') and loss modulus (G'') of the PVP–PEG hydrogel. The frequency dependences of G' and G'' give valuable information on the viscoelastic behavior of the material. When the data cover many decades of frequency, as in Figure 4, a viscoelastic spectrum can be generated. Figure 4 shows the master curves for the G' and G'' moduli obtained at a reference temperature of 20°C for the PVP–PEG blend
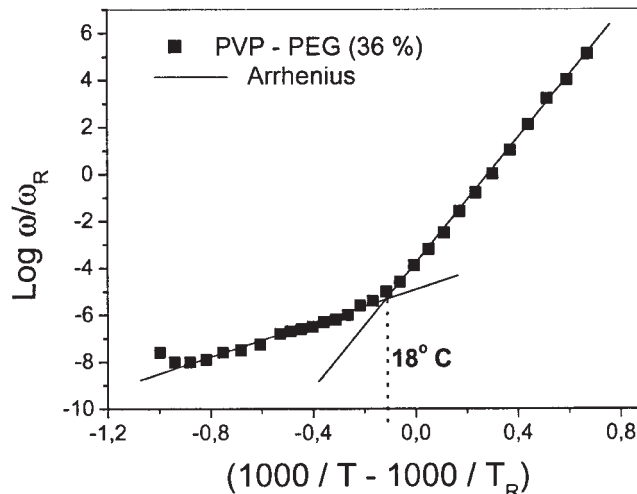

Figure 2 Temperature dependence of the shift factor for PVP blends with 20, 31, 36, or 41 wt % PEG-400.

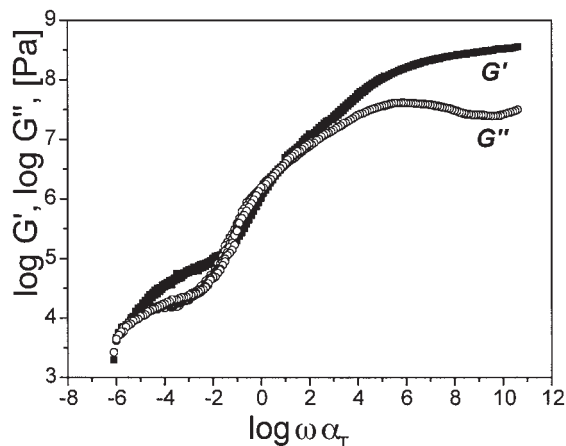**Figure 3** Arrhenius plot of the shift factor for the PVP–PEG (36%) adhesive blend.

Figure 4 Master curves of the dynamic shear moduli, G' and G'', as a function of the frequency for an adhesive PVP blend with 36 wt % PEG-400 containing 11% sorbed water. The reference temperature was 20°C.

containing 36 wt % PEG. With an increase in the frequency, G', gradually increases. Simultaneously, viscous dissipation, represented by G'', also increases. The G'' maximum is usually closely associated with the induced transition to the glassy state.

At first glance, the PVP–PEG blend displays G' and G'' behavior, which is typical of the high-molecular-weight polymers used as PSAs, with a solid-state (or glassy) region at log $\omega a_T > 6$ and a terminal region that transforms to a lower frequency plateau region between log ωa_T values of -2 and -4. However, a close observation of the G' and G'' curves reveals a range of peculiarities that are observed only for PVP–PEG adhesives.

G' is a measure of the elasticity of the adhesive. On the other hand, G'' is associated with energy dissipation during deformation. The greater the G'' value is with respect to G', the more dissipative the adhesive is. In the high-frequency, solid-state region, G' is greater than G''. The values of the moduli lie between 10^7 and 10^8 Pa within this region. With decreasing frequency, the translational mobility of larger polymer segments becomes possible, and the polymer responds to the oscillating shear stress as a viscoelastic material. As a result, the G' and G'' moduli decrease gradually in the so-called transitional region.

It is well known[23] that for monodisperse linear polymers in the terminal (lower frequency) region of the $G'(\omega)$ and $G''(\omega)$ curves, G' is proportional to ω^2 and $G'' \sim \omega$, whereas for structured or crosslinked polymers, the frequency dependence of the G' and G'' moduli is appreciably suppressed and the slopes of the log G/log ω relationships deviate toward much lower values. For PVP blends with 31 or 36% PEG, where a terminal region is observed (Fig. 4), the slopes of the log G'/log ω curves have been found to be 0.37

and 0.55, respectively. The log G''/log ω plots exhibit close values of the slopes (0.30 and 0.43) for blends containing 31 or 36% PEG, respectively. These features imply an increased level of interaction between the blended components, which exceeds conventional van der Waals forces. Moreover, a low-frequency plateau with $G' > G''$ resembles the plateau of rubberlike elasticity. This means that in addition to a high-frequency plateau typical of linear high-molecular-weight polymers, another relaxation process appears at lower frequencies (Fig. 4).

As earlier noted in the discussion of the temperature dependence of G' and G'',[7] the loss tangent goes through a maximum in the middle of the transition region. This means that the PVP–PEG adhesive is much more dissipative than classical PSAs. At the same time, on the basis of the absolute values of G', it is stiffer and provides appreciable cohesion. It is a distinctive feature of the PVP–PEG adhesives that those revealing the best adhesive properties are in the middle of a transitional region at typical test frequencies characteristic of adhesive debonding, whereas all typical (hydrophobic) PSAs demonstrate the best adhesion when they are in the beginning of the high-temperature plateau at the debonding frequencies.[7,9]

As is evident from the curves presented in Figure 4, in the middle of the transitional region, in which the PVP–PEG adhesive has been shown to exhibit large recoverable deformations and the best adhesion,[7–9] the value of elasticity modulus G' is in the vicinity of 10^6 Pa, a value clearly incompatible with the well-known Dahlquist criterion for tackiness,[3] which specifies that an adhesive loses its tack if its elastic modulus at 1 Hz is higher than about 10^5 Pa.

A further decrease in the frequency leads to a reduction in the modulus, and a low-frequency plateau appears on master curves in Figure 4 between 10^{-2} and 10^{-4} Hz; it is characterized by moduli of 10^5–10^4 Pa. As noted previously, we tend to interpret this plateau as an onset of a critical deformation frequency, which is comparable to the relaxation times of the hydrogen-bonded network in the PVP–PEG system. Among conventional hydrophobic PSAs, this plateau appears at much higher frequencies. It is obvious that the atypical behavior of PVP–PEG adhesives in comparison with hydrophobic PSAs is due to the contribution of the hydrogen bonding.

The data in Figure 4 can be treated to obtain a spectrum of relaxation times characterizing the behavior of PVP–PEG adhesive. The relaxation spectrum (H), presented in Figure 5, has been calculated from G', shown in Figure 4, with eq. (4):[23]

$$H(\tau) = AG' \frac{d\log G'}{d\log w}\Big|_{1/w=\tau} \qquad (4)$$
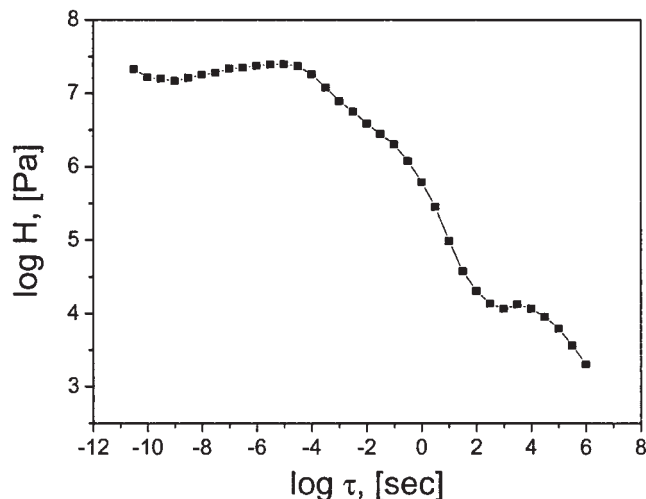
Figure 5 Relaxation spectrum featured for the PVP adhesive blend with 36% PEG at 20°C.

where A is a factor related to the slope of H on a log–log plot, which almost invariably is less than 1 (see ref. 23, p 102). The calculation of the relaxation spectrum from the G'' data has been found to give a similar curve.

The relaxation spectrum in Figure 5 shows three different groups of relaxation times that are typical for the rheological behavior of the PVP–PEG adhesive under shear stress: about 10^{-5}, 1–50, and 1000–3000 s. These values are in fairly reasonable agreement with the results of the direct evaluation of the retardation times of PVP–PEG blends recently measured with a squeeze–recoil test under the conditions imitating the removal of a compressive force in the course of adhesive-bond formation.[26] Two values of the retardation time have been established in this work: the shorter retardation time of 10–70 s and the longer time of 300–660 s. Although the relaxation time of $\sim 10^{-5}$ s most likely refers to the transition from a glassy solid to a viscoelastic state, both longer times are supposed to be associated with the rearrangement of the network of hydrogen bonds.

Figure 6 displays the effect of the PEG content on the dependence of the dynamic moduli G' and G'' on the reduced frequency for PVP–PEG blends containing 11% sorbed water. If the 36% PEG is the reference blend (as a reminder, this blend displayed the best adhesive behavior in both peel[8] and probe tack tests[9]), the PVP blends with 31 or 20% PEG show a similar behavior shifted toward the lower reduced frequencies by about 4×10^2 and 10^9 Hz, respectively (Fig. 6), whereas the blend with 41% PEG displays a maximum dissipation at a reduced frequency shifted by about 10^9 Hz toward higher values. Because the curves presented here are master curves, this is equivalent to saying that similar dissipative processes occur at different temperatures for all blends. It is quite clear from

the curves in Figure 6 that PEG acts as a very good plasticizer of PVP. Furthermore, the lower the PEG content is in the blends, the wider the high-frequency maximum is of G'', which is associated with the transition of PVP–PEG blends from a glassylike state to a viscoelastic state with decreasing frequency (Fig. 6).

Figure 7 exhibits the effect of the PEG concentration on the dynamic viscosity of the PVP–PEG blends, which is defined as the G''/ω ratio. This representation of dynamical mechanical data shows that the PVP–PEG blends are typical non-Newtonian liquids, with the dynamic viscosity climbing gradually with a decrease in the shear frequency. The greater the PVP concentration is, the higher the viscosity is. A characteristic feature of the curves for blends containing 31 or 36 wt % PEG is a pseudo-Newtonian transition that occurs in the vicinity of the middle of the transition area (cf. Figs. 6 and 7): between 10^{-7} and 1 Hz for 36%
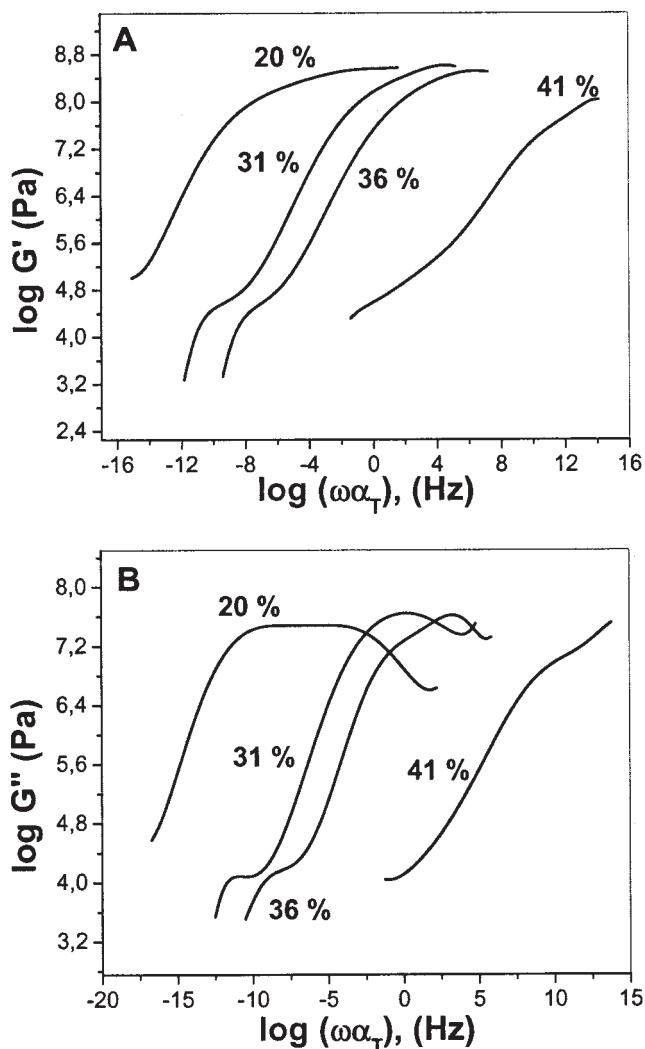

Figure 6 Master curves for the frequency dependence of the dynamic moduli, G' and G'', for PVP blends with 20, 31, 36, or 41 wt % PEG and 11% sorbed water at a reference temperature of 0°C.
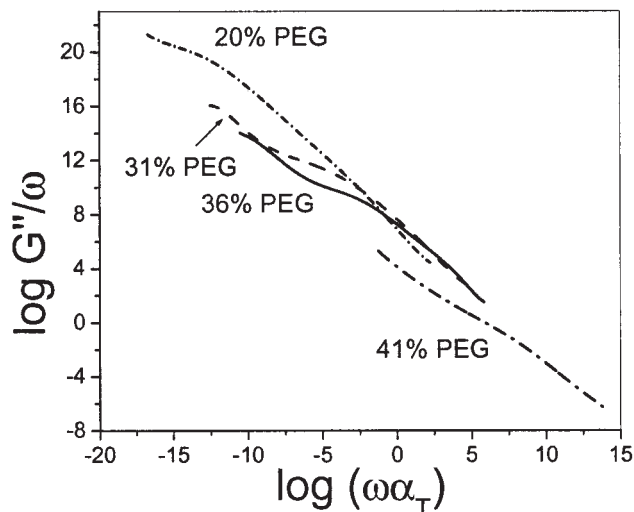
Figure 7 Effect of PEG on the flow curves of PVP–PEG blends containing 11 wt % sorbed water. The reference temperature was 0°C.

Figure 9 Relation of the activation energy (E_a) for viscous flow with the composition of PVP–PEG blends containing 11 wt % water. The reference frequency was 1 Hz.

PEG and within the range of 10^{-9}–10^{-3} Hz for 31% PEG. Similar transitions have been reported to be typical for highly structured polymeric liquids such as liquid-crystalline polymers.[27]

The effect of the water content on the dynamic viscosity curves of the PVP blend with 36% PEG is illustrated in Figure 8. In sharp contrast to the action of PEG, water affects only slightly the dynamic viscosity of PVP–PEG hydrogels. For the blends with 1 or 11 wt % water, a quasi-Newtonian transition takes place between 10^{-5} and 10^{-3} Hz. An increase in the hydration level to 40 wt % leads to a shift of the transition toward 10^2–10^5 Hz. As recently reported,[28] in PVP–PEG blends, adsorbed water is mainly associated with PVP. Within the first hydrated shell of PVP (1–11%), the water molecules are tightly bound,[29] and their effect on the viscosity is comparatively negligible. Above 11% hydration, the water is loosely bound to the monomer units of PVP, and its effect on the reduction of the viscosity is much more appreciable.

The temperature dependences of the viscosity (in Arrhenius coordinates) for PVP–PEG blends are straight lines with slopes, characterizing the flow activation energy. Figure 9 outlines the dependence of the activation energy on the composition of PVP blends with different amounts of PEG at a fixed hydration level (11 wt % water). With the growth of the plasticizer concentration from 20 to 36% PEG, the activation energy decreases gradually from 143 to 119 kJ/mol, demonstrating an abrupt drop at a PEG concentration above 36 wt %. In this way, an abnormally high flow activation energy in PVP–PEG blends argues in favor of strong intermolecular interactions in this system. This fact can also be reasonably explained by the data shown in Figure 4, which demonstrate that at the strain frequency of 1 Hz, the viscoelastic properties of the PVP–PEG blends are more typical of the transition region than of the region of flow.

Rheological properties of PVP–PEG blends under squeezing flow

To gain additional insight into the nature of tack in PVP–PEG blends, we have to consider the pressure-sensitive adhesion as a process in which the structure of the material varies with time and characterize the mechanism of PVP–PEG deformation under conditions resembling the formation of the adhesive bond. Because the PSAs form adhesive bonds under fixed and light pressure, it is reasonable to employ a simple and illustrative squeezing-flow test for this purpose.
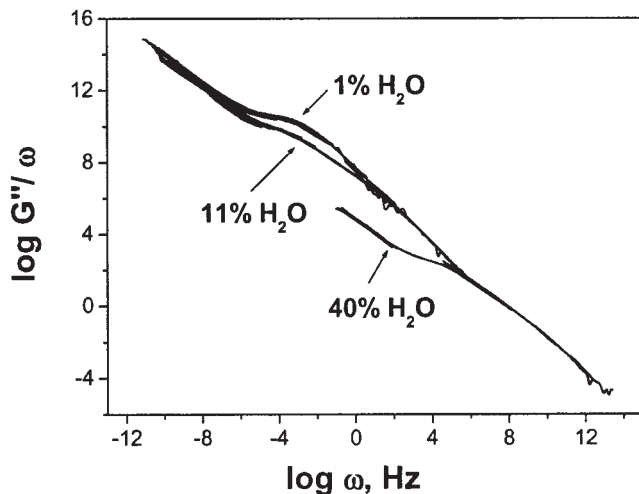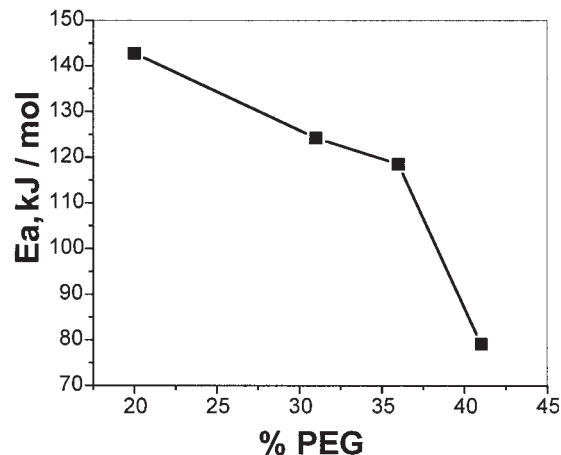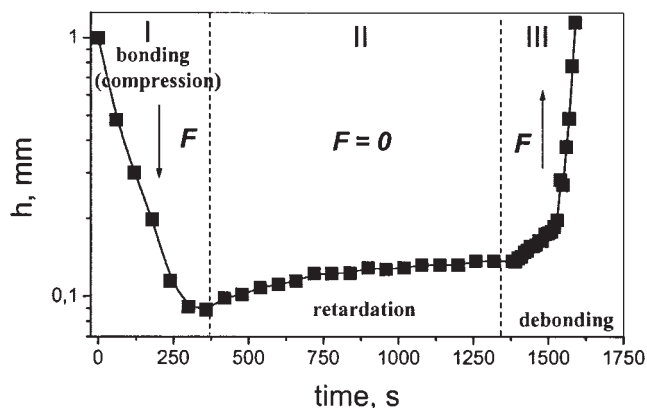

Figure 8 Effect of hydration on the flow curves of PVP–PEG blends containing 1–40 wt % sorbed water. The reference temperature was 0°C.

Figure 10 Typical protocol of squeeze–recoil testing of a PVP–PEG (36%) adhesive film at 40°C. The compressive and debonding forces were 0.2 N.

The process of making and breaking a PSA bond can be divided into three stages: adhesive bonding under compressive force (I), relaxation upon the removal of bonding pressure (II), and rupture of the adhesive bond under a tensile force (III). The squeeze–recoil test provides an adequate characterization of all three stages (Fig. 10). In this work, we focus in detail on the first stage, whereas a short outline of all three stages has been presented in other publications.[26,30,31]

Typical squeezing-flow displacement–time curves for a PVP–PEG adhesive blend under different compressive forces are shown also in Figure 11. As a fixed compressive force is applied to a sample, the gap between the upper and bottom plates of the tester (h), which is equal to the sample thickness, decreases gradually because of a squeezing-out of the sample. A particular feature of the PVP–PEG blends is that the sample thickness does not achieve zero thickness, as is typical of pseudoplastic liquids, but tends toward h_∞; this is due to the existence of a yield stress for the fluid. In this way, the squeezing-flow analysis is a simple way of evaluating an apparent yield stress defined as a critical value of the shear stress at which the material ceases to flow under a fixed compressive force.

As shown in Figure 11, achieving the h_∞ value requires appreciable time. However, squeezing-flow tests that take 4 h (15,000 s) or longer may result in experimental errors because the sample is not protected against the change in hydration under the conditions of the squeezing-flow test. For this reason, we stopped measurements of the h_∞ value in 200–250 min as the changes in h became lower than the accuracy of the measurements, 1 μm. To evaluate the h_∞ values from squeezing-flow profiles, we approximated the curves shown in Figure 11 (in terms of absolute h values) with an exponential decay function of the following type:

$$h = h_\infty + A_1 e^{-t/\theta_1} + A_2 e^{-t/\theta_2} \quad (5)$$

where h is the distance between the dilatometer plates [i.e., the gap (μm)], A_1 and A_2 are equation parameters, t is the experimental time (s), and θ is a characteristic time. As follows from the data listed in Table II, the fitting coefficients, R^2, are quite reasonable. The values of shorter and longer characteristic times, θ_1 and θ_2, describe the processes of elastic response and squeezing flow, respectively.

Because of the obvious proportionality between the measured value of the plateau gap (h_∞) and the applied compressive force, and as follows from eq. (1), the apparent yield stress is nearly independent of the squeezing force. Usually, we had the same values of the apparent yield stress for squeezing forces of 1 and 2 N, whereas for 5 N, the value of the apparent yield stress was typically lower. This fact is quite explicable because under greater squeezing forces, a partial, nonrecoverable breakdown of the material structure can occur, which decreases the cohesive strength of the material characterized by the value of the apparent yield stress. A detailed analysis of the apparent yield stress of the PVP–PEG adhesive blends and of the results of its comparison with the data measured under constant shear stress is presented in the last section of this article.

Figure 12 shows the measured sample height [h (mm)] as a function of time for two identical samples of a PVP–PEG hydrogel of a standard composition (36 wt % PEG-400) subjected to the same stepwise increasing compressive load but with different intervals for the application of the squeezing force. The first sample had a longer time to be squeezed under a fixed force, whereas the second sample was allowed to relax after shorter time periods. Within the first squeezing cycle, both samples were subjected to a compressive force of 1 N, which was applied to an upper plate 6 mm in diameter. The corresponding value of the shear stress was 35 kPa. At the second and third squeezings, the
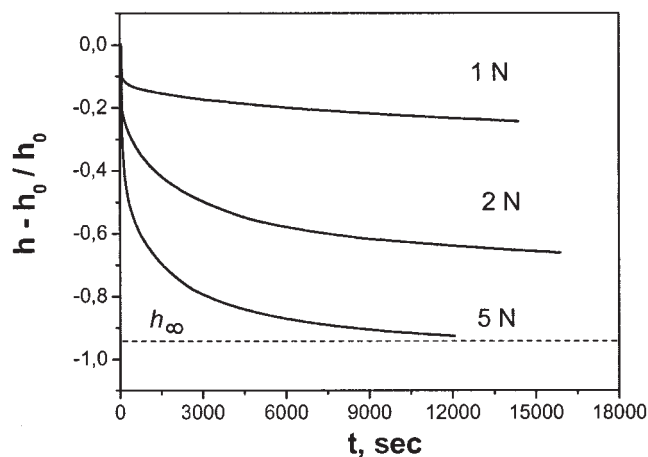

Figure 11 Squeezing-flow profile of a PVP blend with 36% PEG under compressive forces of 1, 2, and 5 N.

TABLE II
Parameters of Fitting the Squeeze-Flow Profiles in Figure 11 with a Function Presented
by Eq. (5) and the Relevant Values of τ_y

Force (N)	h_∞ (μm)	A_1	A_2	θ_1	θ_2	R^2	$\log \tau_y$ (Pa)
1	675	62	124	133	8686	0.99	4.20
2	336	176	331	405	4345	0.99	4.20
5	69	356	600	2592	101	0.99	3.99

compressive force was increased to 2 and 5 N, respectively.

The theory of parallel-plate rheometry is based on a number of simplifying assumptions.[32] In particular, the inertial terms imposed by polymer elasticity in the equations of motion are neglected, and the velocity distribution is assumed to depend on the spatial variables in a certain way. Bird et al.[33] gave the derivation of the Stefan equation relating the force to the speed of the upper plate having radius R for a Newtonian fluid:

$$F = \frac{3\pi R^4 \eta [-dh/dt]}{8h^3} \quad (6)$$

where η is the fluid viscosity. Integrating eq. (6) for a constant force yields the following equation describing the kinetics of the change in h:

$$\frac{1}{h^2} = \frac{1}{h_0^2} + \frac{16Ft}{3\pi R^4 \eta} \quad (7)$$

However, the instantaneous elastic response cannot be neglected at the onset of the flow, so if $1/h^2$ values are plotted versus time, the first few points will not lie on a line intersecting the vertical axis at the initial gap height, $1/h_0^2$. If the data approach a straight line, this

can be considered evidence that the slope can in principle be used to calculate the viscosity.

The kinetic profiles presented in Figure 12 provide information on the viscoelastic properties of the hydrogel. The higher the squeezing stress is, the more deformed the PVP–PEG hydrogel is. The deformation of the hydrogel under a squeezing flow is partly recoverable. As the compressive force is removed, the sample returns more or less to its initial shape. The profile of the squeeze recoil is indicative of the elastic contribution and relaxation properties of the material.

Figure 13 replots the kinetic curves shown in Figure 12 in the coordinates of eq. (7). This equation holds for Newtonian liquids, for which the slope in the linear region is inversely proportional to the viscosity. In our experiments, the slope of the $1/h^2$–t curve increases with increasing squeezing force, indicating the dependence of the viscosity on the applied stress. The variation of the viscosity with the shear stress is evidence of the non-Newtonian behavior of a liquid. Indeed, an increase in the compressive force to 5 N causes the linear region of the curve to vanish (data are not shown). Consequently, the PVP–PEG hydrogel should be treated as a non-Newtonian, power-law liquid.

The flow curves of polymer liquids have two distinct regions: the Newtonian region and the power-law region. The Newtonian region is observed at very low shear rates, at which the viscosity is independent of the
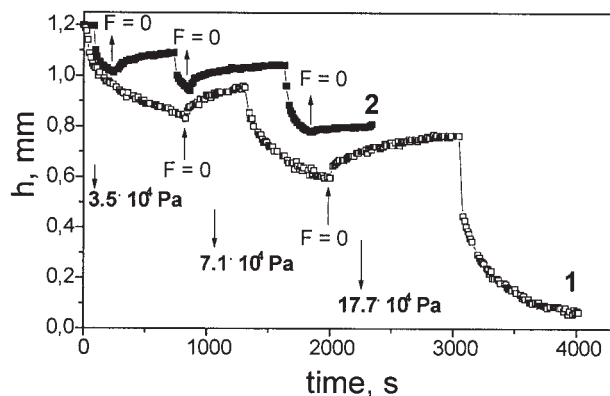

Figure 12 Kinetics of PVP–PEG hydrogels squeezing under repeating stepwise increasing compressive load, followed by retardation. h is the gap between the bottom and upper plates of a squeeze–recoil tester and is equal to the thickness of the specimen (mm). The values of the compressive stresses are shown.
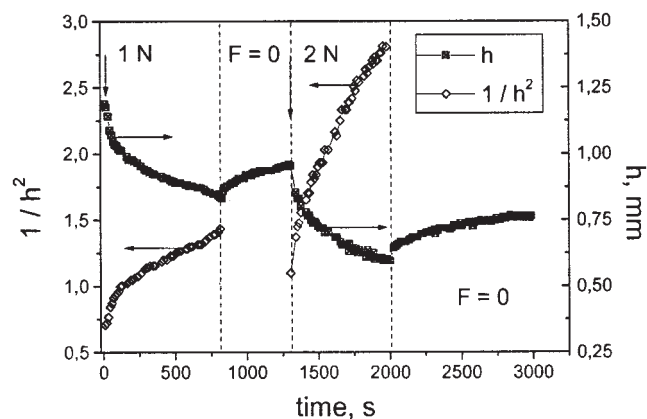

Figure 13 h (mm) and $1/h^2$ versus the time for squeezing of PVP–PEG hydrogels under a fixed force of 1 or 2 N. According to eq. (7), the slope of the $1/h^2$–t relationship outlines the apparent shear viscosity of the material.
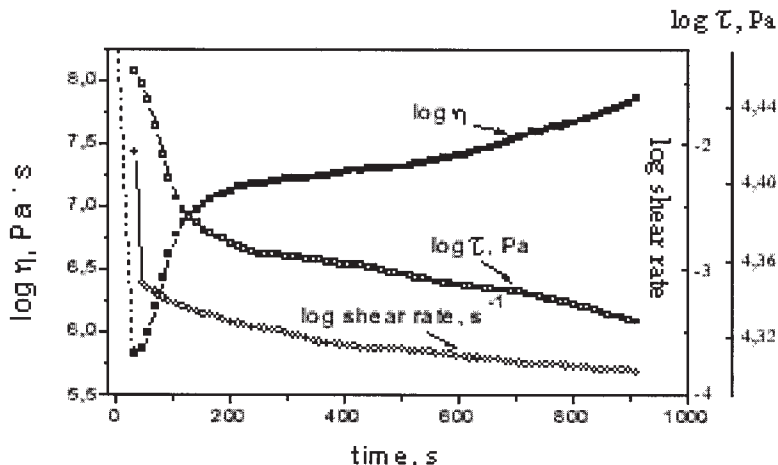
Figure 14 Dynamics of the shear stress, shear rate, and apparent shear viscosity behavior for PVP–PEG (36%) hydrogels over the time of squeezing under a compressive force of 1 N.

shear rate. The power-law region is the region in which the viscosity decreases with an increasing shear rate to a limiting slope defined by a power-law index, n.

For a power-law liquid

$$\tau = k\dot{\gamma}_R^n \tag{8}$$

At a constant squeezing force, τ_R and the shear rate, $\dot{\gamma}_R$ (on the rod edge), can be calculated as follows:[34]

$$\tau_R = \frac{n+3}{2} \times \frac{hF}{\pi R^3} \tag{9}$$

$$\dot{\gamma}_R = \frac{2n+1}{n} \cdot \frac{(-\dot{H})R}{h^2} \tag{10}$$

where $\dot{H}$ is the velocity of the moving plate, R is the radius of the upper plate, and n is the exponent of the power law.

From eqs. (9) and (10), it is obvious that the shear rate and stress in the gap decrease in the course of an experiment because h decreases continuously under the compressive force.

Equation (6) was adapted to the power-law fluid by Scott[33] as follows:

$$F = \left(\frac{\eta \pi R^{n+1}}{n+3}\right)\left(\frac{2n+1}{2n}\right)\frac{(-dh/dt)^n}{h^{2n+1}} \tag{11}$$

which simplifies to eq. (6) for $n = 1$. The n value represents the deviation of the polymeric liquid from the Newtonian behavior, ranging from 1 to 0. For the majority of commercial high-molecular-weight polymers, n varies between 0.6 and 0.3. Lower values of n are typical of highly structured fluids.[35]

For the power-law liquids, the shear stress and shear rate can be calculated at different times of the

squeezing experiment from the corresponding h values measured with eqs. (9) and (10). The ratio of the shear stress to the shear rate gives the viscosity. n represents the slope of the plot of $\log(-dh/dt)$ versus $\log h$.

Equation (7) is inapplicable for evaluating the viscosity of non-Newtonian liquids, and so the specific software offered by Gordon and Shaw,[36] based on eqs. (9) and (10), has been employed for the calculation of the shear stress and shear rate. A power-law behavior of the hydrogel is assumed, and the n index is allowed to vary with the underlying shear rate. As the shear stress and shear rate are found, the apparent shear viscosity can be easily obtained as their ratio. The results are illustrated in Figures 14 and 15.

Figure 14 illustrates the rheological changes occurring in the PVP–PEG adhesive blend under the conditions corresponding to the formation of an adhesive bond. Before the experiment starts, because no squeezing force is applied, both the shear stress and shear rate are zero, and the apparent shear viscosity is extremely high (Fig. 14); this is typical of polymers pos-
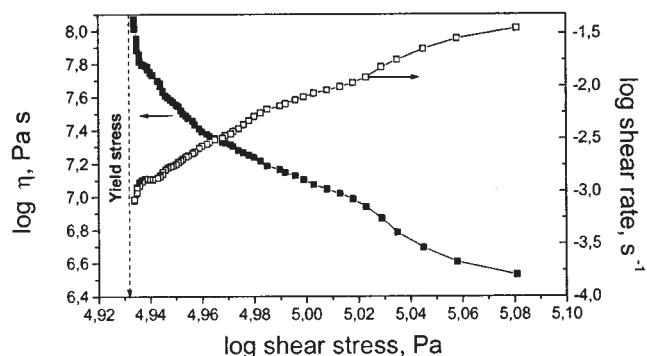

Figure 15 Flow curve of PVP–PEG hydrogels subjected to a fixed squeezing force of 5 N.

sessing a yield stress. However, under a fixed compressive force, the shear stress and shear rate grow almost instantaneously to the values defined by eqs. (9) and (10), whereas their ratio, the apparent shear viscosity, drops. Because the compressive force has been kept constant, the shear stress decreases gradually, following the pattern given by decreasing h [eq. (9)]. The shear rate, outlined by the slope of the kinetic profiles presented in Figure 11 [eq. (10)], decreases as well, whereas the apparent viscosity increases, tending toward infinity at considerably longer times when the yield stress is achieved. The significance of the data in Figure 14 is that the squeeze flow of the hydrogel is only appreciable in the early stages of the compression process (within the first 3 min under a compressive stress of 35 kPa). With an increase in the compressive stress to 177 kPa (squeezing force = 5 N), the duration of the initial region of growth of the viscosity has been shown to decrease to 78 s, whereas the minimum magnitude of the logarithm of the apparent shear viscosity increases from 5.8 to 6.5 in comparison with that of the sample under a 1 N squeezing force.

It is well recognized that the phenomenon of tackiness features a high shear flow of an adhesive material under a compressive force. In the process of adhesive bonding, a high, liquidlike fluidity of the adhesive is required to wet the surface of a substrate (which may be rough) over a few seconds while a compressive force is applied. However, to form a tough adhesive bond, the shear flow of the adhesive material should be short-term. As shown by the curves in Figure 14, for the PVP–PEG adhesive, the shear rate is high for a few seconds upon the application of the compressive force, and the lower the compressive force is, the shorter the period of flow is. This means that for proper pressure-sensitive adhesion, light compressive forces are preferred.

Plotting the shear rate and apparent shear viscosity against the corresponding shear stress values (displayed in the figure), we have obtained the PVP–PEG flow curve, which is illustrated in Figure 15 for the hydrogel squeezed under a compressive force of 5 N. The lack of a steady-state region on the curves, when the shear viscosity is independent of the shear stress, is evidence of a non-Newtonian flow within the shear stress range applied in the loading cycle of our experiment. The divergence of the apparent viscosity for log $\tau < 4.93$, that is, an apparent yield stress close to 10 kPa, accompanied by the corresponding drop in the shear rate (Fig. 15), is a sign that the apparent yield stress has been achieved in this region.

The non-Newtonian behavior of the squeezing flow is due to the impact of the elastic contribution. According to Laun's empirical criterion,[34] the contribution of polymer elasticity to the squeezing flow is only negligible within a region of apparent strain in which
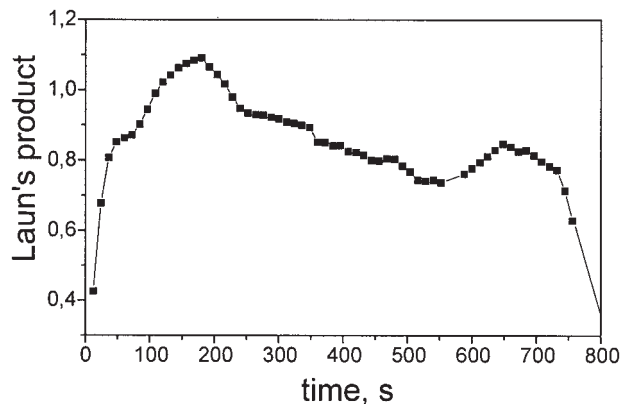

Figure 16 Momentary shear strain versus the running time for PVP–PEG hydrogels subjected to a squeezing force of 5 N.

the product of the instantaneous shear rate by the time is larger than 40. As follows from the data in Figure 16, this criterion never holds for PVP–PEG hydrogels even for the maximum compressive force applied, when the shear rate is highest. The Laun criterion is in principle unattainable for PVP–PEG hydrogels because at higher shear rates the running time is too low, whereas at longer times the shear rate decreases, tending to zero because of the yield stress. That is why the shear viscosity established in this work with the squeezing-flow test is treated as the apparent shear viscosity. Correspondingly, the yield stress is considered an apparent quantity both because of the aforementioned nonuniformity of the shear stress under the conditions of squeezing flow and because it is found by the analysis of the dependence of the apparent shear viscosity on the shear stress and shear rate. However, even though the apparent shear viscosity and the apparent yield stress cannot be treated as true properties of the adhesive material, nevertheless they are valuable and illustrative characteristics of the rheological behavior of the adhesive material over the course of a stress–strain history resembling that of adhesive bonding.

To understand how far away the squeezing flow of a PVP–PEG hydrogel deviates from the Newtonian behavior, the assessment of n can be useful. n is defined by the slopes (tan α) of the relationships shown in Figure 13 for the squeezing forces of 1 and 2 N [tan $\alpha = (2n + 1)/n$]. As Figure 17 demonstrates, within a wide range of sample thicknesses and gap values, the data lie on straight lines, whereas the points relating to a high degree of compression drop out because of the yield stress. The lines for both compressive forces are almost parallel, indicating the close values of the n index. As is evident from the data listed in Table III, the n values obtained for the PVP–PEG hydrogel squeezed under different compressive forces average to $n = 0.1206 \pm 0.0054$ ($p = 0.04661$), both with fresh
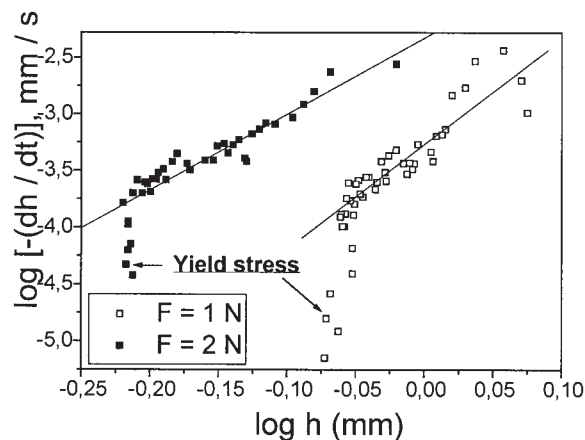
Figure 17 Log–log plot of the squeezing rate ($-dh/dt$) versus the thickness of the sample [h (mm)]. The compressive forces are indicated.

Figure 18 Shear strain (γ) of the PVP–PEG (36 wt %) adhesive under a fixed shear stress as a function of time.

samples and with samples previously compressed under smaller loads. The independence of n of the squeezing force and testing regime implies that the n value is a material parameter. Although Newtonian liquids are reported to possess an n index close to 1, the power-law liquids typically have n values ranging from 0.6 to 0.3. The value of $n = 0.12$ found in this study signifies that the PVP–PEG hydrogel deviates drastically even from the behavior of the majority of power-law liquids. The implication of this fact is that the elastic contributions to the squeeze flow of the PVP–PEG adhesive hydrogel can never be ignored.

Yield stress

As a result of a nonuniform stress distribution over the surface of the squeezing plate, the squeezing-flow technique enables only a rough evaluation of the yield stress.[20] For a more accurate characterization of the yield stress as a material constant for the PVP–PEG system, the yield stress has also been measured with a parallel-plate shear plastometer under different values of the applied shear stress. As follows from the data presented in Figure 18, under a shear stress of 1200 Pa, which is lower than the apparent yield stress of the PVP–PEG adhesive, no shear flow occurs after an initial section of the shear strain/time curve, referring
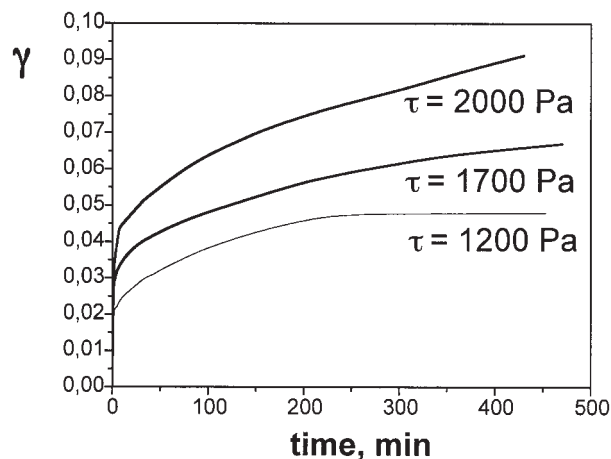
to the elastic response of the adhesive material to the applied load. If the applied shear stress is above a value of the yield stress, which has been found to be between 1200 and 1500 Pa, the adhesive material reveals unrecoverable plastic deformation. The difference between the values of the apparent yield stress determined by the squeezing-flow test and the true yield stress evaluated with constant stress rheometry is discussed next.

As for the data of the squeezing-flow test, the apparent yield stress can be calculated from the squeezing-flow profiles presented in Figures 11 and 12 with eq. (1) and the minimum value of h (h_∞; Fig. 11). The measured value of the apparent yield stress is a decreasing function of both the PEG content and concentration of sorbed water (Figs. 19 and 20). The composition dependence of the apparent yield stress in Figure 19 follows the pattern shown in Figure 9 by the plot of the flow activation energy versus the PEG
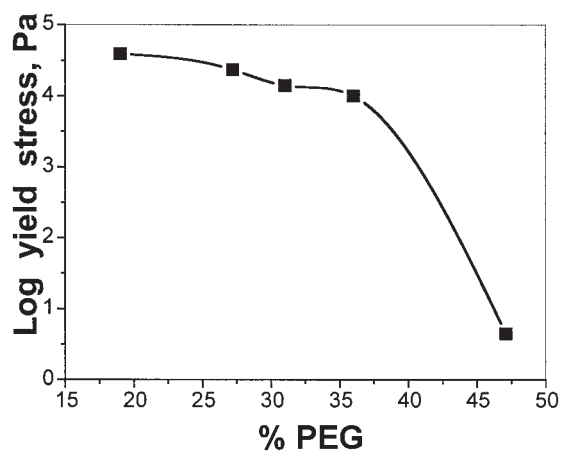
TABLE III
n Values Inherent in PVP–PEG Hydrogels Squeezed under Various Values of F

F (N)	n	R	p
0.5	0.036	0.8635	<0.0001
1	0.138	0.8626	<0.0001
2	0.212	0.9417	<0.0001
5	0.097	0.9831	<0.0001

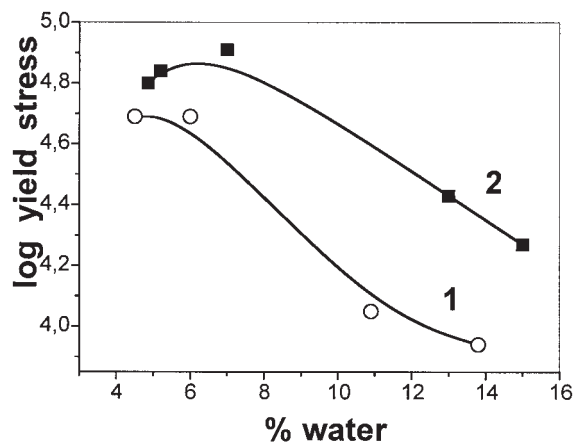**Figure 19** Effect of the PVP–PEG composition on the value of the apparent yield stress in PVP–PEG blends.

Figure 20 Effect of the water content on the apparent yield stress of PVP–PEG (36%) hydrogels prepared by the casting of (1) ethanol and (2) aqueous solutions followed by drying. The dry films were then allowed to absorb water.

content. In a similar way, the apparent yield stress has been found to decrease with an increasing hydration level of the PVP–PEG hydrogels (Fig. 20). The value of the apparent yield stress is also affected by the method of film preparation. As is evident from the data in Figure 20, the cohesive toughness (expressed in terms of the yield stress) is appreciably higher if the samples are prepared by the dissolution of PVP and PEG in water, in comparison with their ethanol solutions.

As shown by a comparison of the data shown in Figures 18–20, the value of the apparent yield stress measured with the squeezing-flow test is appreciably higher than the true value determined with the shear plastometer under a constant shear stress. The value of the true yield stress is about four times less than the apparent yield stress for the PVP–PEG adhesive blend with 36% PEG. The difference between the true and apparent yield stresses is greater than the factor of 0.67 reported by Laun.[22] This fact is explicable in view of both the nonuniformity of the shear stress at the surface of the moving rod of the squeezing-flow tester (accounted for by Laun) and the limited time of measure in the course of squeezing. In this work, we are mostly interested in gaining insight into a molecular interpretation of the yield stress in PVP–PEG systems and in understanding the contribution of hydrogen bonding to this property. This requires a qualitative examination of the effects of the composition, water content, and molecular weight of PVP on the yield stress. We believe that the values of the true and apparent yield stresses, despite their quantitative difference, are similarly affected by the composition and hydration of the PVP–PEG system. The squeezing-flow test is more convenient for the qualitative assessment of these effects. The major advantage of the squeezing-flow test in comparison with a stepwise loading with a fixed yield stress is that in the squeez-

ing-flow experiment, the moment of onset of rapid growth of the viscosity can be accurately established (see the flow curve in Fig. 15) and represents the time when the material ceases to flow.

The occurrence of a yield stress is a characteristic feature of crosslinked or strongly interacting, structured polymers. Commodity polymers do not normally show a yield stress. Flow curves shown for PVP–PEG hydrogels in Figures 14 and 15 have been found to be incomplete. If the shear stress is varied within a wider region, the flow curve has a specific two-step shape presented in Figure 21. Similar two-step flow curves are reported to be also typical of liquid-crystalline polymers.[27] This curve is thought to reflect the coexistence of two types of networks in PVP–PEG hydrogels.[7,37] The first network is an entanglement network due to the presence of high-molecular-weight PVP. The second network is a physical network of PEG crosslinks due to the hydrogen bonds formed between the PVP repeat units and the PEG terminal hydroxyl groups.

In liquid-crystalline polymers, the two steps of the flow curve are supposedly related to the orientation of mesogenic macromolecular associations (domains) along the direction of shear at a comparatively low shear stress and to the flow of the liquid-crystalline structure at a higher shear stress (monodomain flow).[27] Although the PVP–PEG blends reveal no liquid-crystalline structure, they do exhibit an optical anisotropy as a tensile stress is applied.[7] At a low shear stress, the PVP–PEG blend is fully crosslinked through hydrogen bonds and entanglements and does not flow. The drop in viscosity for the left descending branch of the flow curve in Figure 21 implies most likely the disentanglements of PVP chains. In the disentangled state, the material starts to flow like a Newtonian liquid with a viscosity that is independent of the applied shear stress. However, as the shear stress
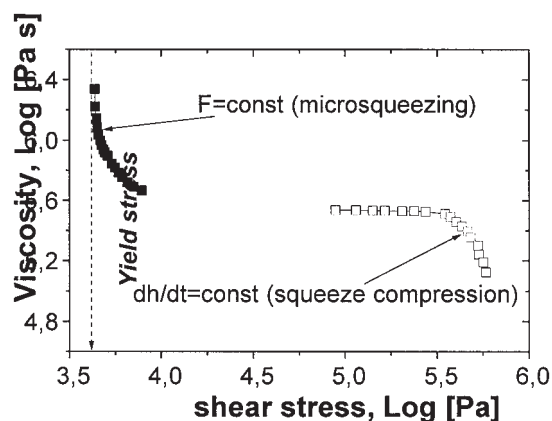

Figure 21 Flow curves for PVP–PEG (36%) hydrogels at low (microsqueezing) and high (squeeze compression) shear stress values.
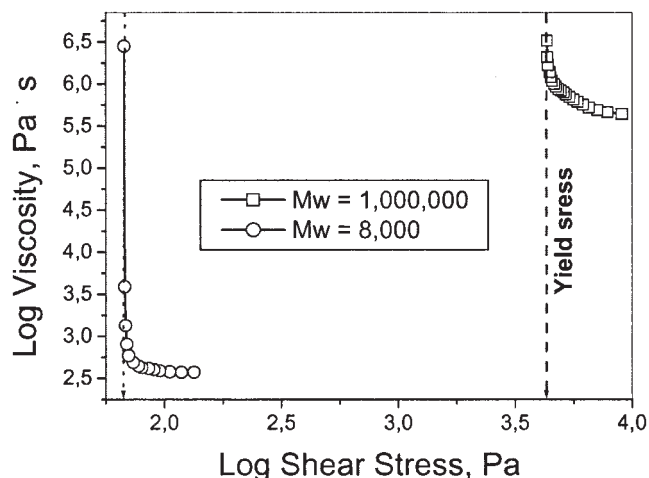
Figure 22 Effect of the molecular weight of PVP on the flow curves for PVP–PEG (36%) hydrogels for PVP with a weight-average molecular weight of 1×10^6 or 2–8×10^3 g/mol.

becomes comparable to the strength of the hydrogen-bonded network, the viscosity drops again (right descending branch), and the yield stress vanishes.

As shown by Ahmad and coworkers,[38,39] the behavior of the yield stress in PVP solutions is indicative of the contributions of hydrogen bonding and the entanglements of polymer chains. To characterize the respective contributions of the hydrogen-bonded and entanglement networks to the flow curve in Figure 21, let us consider the dependence of the apparent yield stress on the molecular weight of the PVP chains (Fig. 22). As follows from the results of the uniaxial extension of PVP–PEG blends under tensile stress[7] within a region of large strain, the average molecular weight between neighboring entanglements of PVP chains is about 220,000 g/mol for adhesive PVP blends with 36% PEG-400.[37] It is clear that the contribution of the network of PVP chain entanglements can be essentially reduced or even eliminated with a PVP of a molecular weight lower than 220,000 g/mol.

The occurrence of a clearly pronounced apparent yield stress for the blends of higher and lower molecular weight PVPs confirms the important role of their network structure (Fig. 22). The strength of the network provided by the high-molecular-weight PVP is approximately 60 times greater than that of the lower molecular weight fraction. Accordingly, the steady-state apparent shear viscosity within the Newtonian regime is about 1200 times higher for the blend of high-molecular-weight PVP. The blends of higher molecular weight PVP dissipate more mechanical energy for the deformation of macromolecules, thus stabilizing the network formed by the PVP–PEG hydrogen bonds. The fact that both blends exhibit a yield stress indicates most likely that the yield stress is a property of the hydrogen-bonded network. Actually, although

the entanglements of the PVP chains are dramatically affected by the PVP molecular weight, the effect of the PVP chain length on the hydrogen bonding with PEG is much less pronounced.

Additional evidence in favor of attributing the origin of the yield stress to the hydrogen-bonded network can be obtained from its temperature dependence presented in Figure 23. To measure the apparent yield stress as a function of temperature, the hydrogel was squeezed under a fixed compressive force until a limiting value of the gap between the plates of the squeezing-flow tester (h_∞) was achieved, and then the temperature was elevated at a heating rate of 0.5°C/min. It is well known that the hydrogen bonds become looser and eventually rupture with a rise in temperature. As is obvious from Figure 23, an increase in the temperature to 40°C causes no effect on the apparent yield stress. The following increase in the temperature leads to a gradual reduction of the apparent yield stress. At temperatures greater than 100°C, the apparent yield stress drops by 1 order of magnitude. Finally, as the temperature is raised up to 135°C (where PVP–PEG hydrogen bonds do not exist any longer), the yield stress vanishes altogether.

CONCLUSIONS

Although viscoelastic properties of PSAs in the process of adhesive-bond failure have been much studied and are comparatively well understood, the rheological behavior of these adhesives at the stage of adhesive-bond formation remains scantily known. The squeezing-flow method, employed in this work, provides adequate rheological characterization of the behavior of the PSAs in the process of adhesive bonding as the adhesives are subjected to a fixed compressive force for some period of time. The results presented in this article show that an adhesive blend of high-mo-
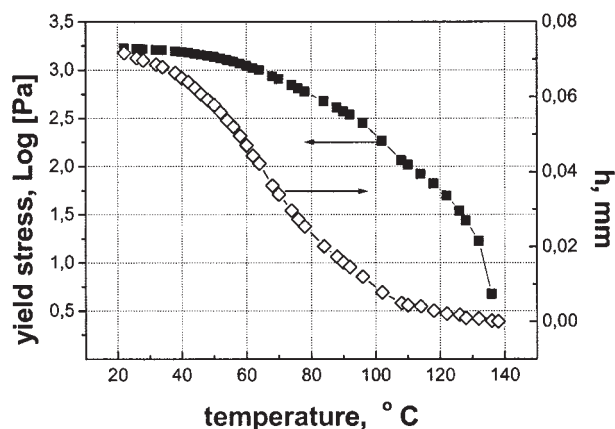

Figure 23 h and apparent yield stress versus the temperature for PVP–PEG (36%) hydrogels. The heating rate was 0.5°C/min.

lecular-weight PVP with short-chain PEG-400 can be treated as a non-Newtonian liquid with an *n* value of approximately 0.12, which is typical of very structured fluids. A particular feature of the PVP–PEG blends is the occurrence of a yield stress, which arises because of the formation of hydrogen bonds between proton-donating terminal hydroxyl groups of PEG and complementary electron-donating carbonyl groups in PVP repeat units, as established earlier by FTIR spectroscopy. However, we find that the value of the yield stress is dependent not only on the local hydrogen-bonding structure but also on the presence of entanglements in the high-molecular-weight PVP. If entanglements are suppressed, the yield stress is still observed, but its value is significantly lower. Because linear entangled polymers normally exhibit no yield stress, we have come to the conclusion that the existence of entanglement networks in PVP–PEG blends has a stabilizing effect on the network of hydrogen bonds.

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