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SMALL AND LARGE STRAIN MECHANICAL PROPERTIES OF A MODEL HYDROPHILIC ADHESIVE GEL

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Introduction

While most commercial soft adhesives are based on hydrophobic components, this is no longer true for the specific application of skin adhesives. Due to their low toxicity and ready absorption of moisture, hydrophilic gels are often used.

The requirement of hydrophilicity implies the presence of polar components and often of hydrogen bonding. Furthermore properties of such gels are highly dependent on water content.

Although the mechanical and adhesive properties of hydrophobic adhesives have been extensively investigated, much less is known of their hydrophilic counterparts. It is expected that the presence of a network of hydrogen bonds will greatly alter the deformation properties of such an adhesive both in small and large strains.

Adhesion tests performed with a probe method[1] showed an uncharacteristically high sensitivity to the velocity of removal of the probe, with a sharp transition from detachment by fibril formation at low probe velocity to brittle fracture at high probe velocity. Furthermore the small strain storage part of the elastic modulus G', was close to 1 MPa, in the frequency regime where significant pressure-sensitive-adhesion was observed, result in blatant disagreement with the well-known Dahlquist's criterion.

Experimental

PVP (Kollidon K-90), $M_w = 1{,}000{,}000$ g mol^{-1}, $M_n = 360{,}000$ g mol^{-1}, glass transition temperature $T_g = 178^o$ C (BASF), and PEG of molecular weight 400 g mol^{-1}, $T_g = -70^o$ C (Carbowax Sentry NF, Union Carbide Corp.) were used as received.

For the DMA tests The PVP-PEG samples were prepared from solutions in ethanol, dried and conditioned in order to have a water content of 11 wt.%. The dynamic mechanical properties of the adhesives in the linear viscoelastic regime were measured on a parallel plate rheometer RDA II from Rheometrics. The deformation rate was varied between 0.01 and 100 rad/s and the amplitude of deformation was chosen to stay in the linearity regime, i.e. between 0.1 and 1% depending on the temperature. Master curves as a function of temperature were constructed by applying the time-temperature equivalence. The reference frequency of 1 Hz was chosen for all the blends examined.

The 700 µm thick films of PVP - PEG blends for the tensile tests were obtained by casting the ethanol solution onto the siliconized surface of a polyethylene terephthalate (PET) PEBAX - 600 release liner (60 µm in thickness), dried and conditioned to an average water content of 6.5 ± 0.8 wt. %. Upon drying, the PVP - PEG adhesive films were covered by the second sheet of the PEBAX-600 release liner. From this point on the term “hydrogels” is used to designate equilibrium hydrated PVP - PEG blends.

The tensile stress-strain behavior of the adhesive films was studied with an Instron 1222 Tensile Tester at ambient temperature. Dumbbell-shaped samples of the total length of 21 mm with a nip-to-nip distance of 10 mm were cut from rectangular films of 0.5 - 0.7 mm in thickness. The width of a necked region was 5 mm. The tensile strength of the samples was determined at fixed cross head speed ranging from 10 to 100 mm per minute. The nominal tensile stress was defined as a stretching force normalized by the original cross-section area of the sample. More details on sample preparation and experimental conditions can be found in a forthcoming publication[2].

Results

The viscoelastic properties of the hydrogels in small strain have been well characterized and a temperature scan of G' and G" at 1 Hz is shown for the sample with 11% water content and 36 wt% PEG. It is important to note that the maximum in tan δ usually associated with the glass transition temperature occurs at a temperature which is 20°C higher than the T_g measured by DSC and for a range of values of G' around 1 MPa. In other words the gel shows a highly dissipative behavior in a regime where a high molecular mobility is expected at the monomer level.

It is also important to note that the gel displays its best adhesive properties in that window of highly dissipative behavior. A variation in PEG content (with the water content kept constant) shifts the maximum in tan δ to higher or lower temperatures. Finally, it is important to note that the storage part of the small strain modulus G' is very sensitive to the PEG content and is given in Table I for various PEG contents.

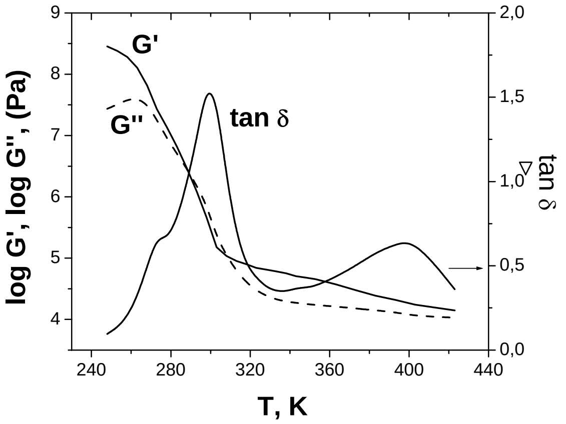

Figure 1: G' and G" and tan δ at a frequency of 1 Hz in oscillatory shear.

Table 1. Small strain moduli G' (MPa) obtained with the rheometer at a frequency of: f = ω/2π

%PEG	0.01 Hz	0.1 Hz	1 Hz
31	9	22	52
36	0.22	0.92	3.3
41	0.013	0.028	0.048

If the same gel is now tested in tension and up to large strains, the results are even more informative.

Figure 2 shows the stress-strain curves for a series of gels with varying PEG content and a constant water content fixed at 6.5 %.

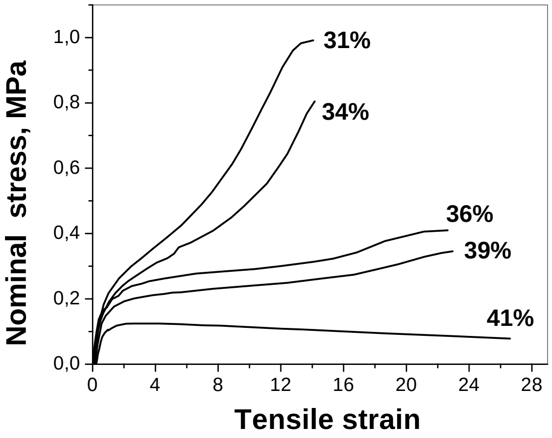

Figure 2: Stress-strain curves of PVP-PEG blends containing 6.5% water. Applied crosshead velocity: 20 mm/min ($d\varepsilon/dt = 0.033\ s^{-1}$).

It is quite clear that, on the contrary to the oscillatory shear data, the initial modulus of the stress-strain curve does not appear to be much affected by the change in PEG, although the large strain behavior becomes dramatically different with a relatively small change in PEG content. The magnitude of this effect can best be shown by analyzing the tensile data in light of existing models for rubber elasticity.

The molecular theory of the deformation of rubber elastic networks has been recently reviewed and generalized by Rubinstein and Panyukov[3]. They divide the elastic free energy essentially in two components: the component due to entanglements and that due to crosslinks. For small strains, the elastic modulus becomes simply the sum of the entanglement (G_e) and crosslink (G_c) contribution. For large strains and uniaxial extension their model predicts:

$$\sigma_n = \left[G_e + \frac{G_e}{0.74\lambda + 0.61\lambda^{-1/2} - 0.35}\right]\left(\lambda - \frac{1}{\lambda^2}\right) \qquad (1)$$

where λ is the extension ratio l/l_0 and σ_n is the nominal stress F/A_0.Figure 3 shows the data of figure 2 plotted as a so called Mooney ratio, i.e. the stress normalized by ($\lambda - 1/\lambda^2$) in the range of λ varying from 2 to 10. The lines are the best fit using equation 1. As one can see fits are quite good in the intermediate deformation rate region. For the lowest PEG contents, a strain hardening at high extensions is observed, which cannot be accounted for by the theory of rubber elasticity.

From the fits one can extract the two parameters of the model G_c and G_e for all compositions.

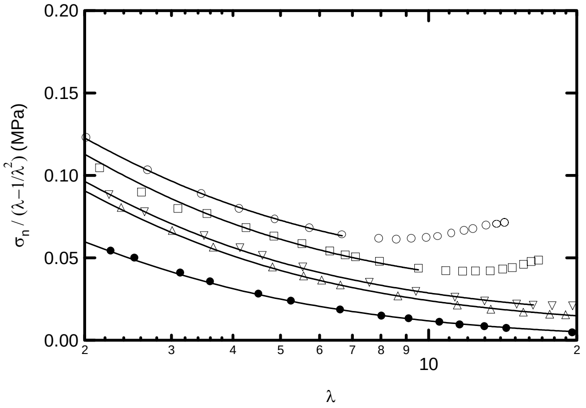

Figure 3: Mooney ratio as a function of extension ratio. ● 41%PEG; △ 39% PEG; ▽ 36% PEG; □34% PEG; ○ 31%PEG.

These values are plotted on figure 4 as a function of PEG content. It is immediately apparent that, in large strain extension, the PVP-PEG hydrogels behave as weakly crosslinked systems when the PEG content is below 41wt%. In that regime the modulus is the sum of an entanglement contribution (nearly constant with PEG content) and a crosslining contribution which decreases linearly with increasing PEG content and vanishes for 41% PEG.

An interesting cross check of the validity of the model is the comparison between the value of $G = G_c + G_e$ and the value of the initial slope of the stress-strain curve E.

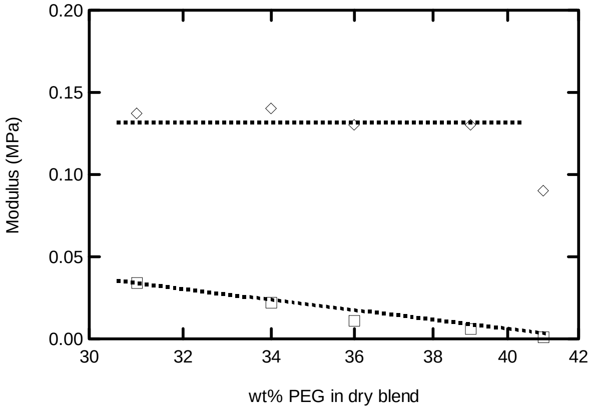

Figure 4: Crosslink G_c (□) and entanglement G_e (◇) contributions to the large strain modulus as a function of % PEG in the blend.

The ratio E/G is shown on figure 5 as a function of PEG content. In principle that ratio should be equal to 3, independently of the PEG content. However given the uncertainties in the absolute value of the measurement the agreement is quite good.

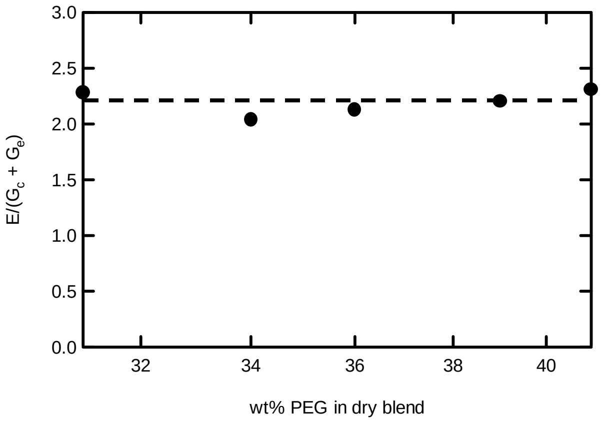

Figure 5: Ratio $E/(G_c+G_e)$ as a function of PEG content

On the other hand the ratio of the value of $G'/(G_c+G_e)$, where G' is measured at a deformation rate of 0.033 s^{-1} corresponding to a drawing rate of 20 mm/min, is given on figure 6. Not only the values obtained with the two different techniques are very different but more importantly the effect of increasing the PEG content is dramatically different at deformations below 1% and at strains of 100-900%.

Discussion and Conclusion

Based on the previous investigations of the structure of the PVP-PEG hydrogels, the following interpretations can be given to the results obtained here. The hydrogel responds as a superposition of two networks, an entanglement network due to the presence of high molecular weight PVP and a physical crosslink network due to the hydrogen bonds established between the PVP and the PEG hydroxyl groups.

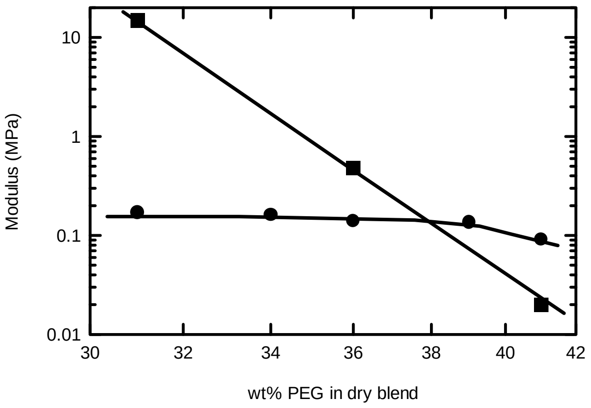

Figure 6: Small strain modulus G' (■) and large strain modulus: G_c+G_e (●) as a function of PEG content

At small strains the hydrogen bonds form a tight network bridging the PVP chains with the OH terminal groups of the short PEG chains. However that tight network cannot be reformed very rapidly, once broken and even at very low deformation rates, the blends flow above a certain level of deformation. Once the material starts to flow, it behaves like a very weakly crosslinked viscoelastic rubber. Using a rubber elasticity model one can interpret the value of G_c as a density of elastic strands ν. From Figure 6 one can conclude that ν decreases linearly with increasing PEG content from a maximum density of 8.3 x 10^{24} strands/m^3 (given as a first approximation from $\nu = G_c/kT$). This result gives an average molecular weight between crosslinks of 72 kg/mole for the 31% PEG. However the best PSA properties are observed for the 36% PEG blend where the average molecular weight between physical crosslinks is now 220 kg/mole.

It should be noted however that the crosslinks created by hydrogen bonding are not permanent but temporary. If the tensile tests are performed at different strain rates, different results are obtained and the polymer displays very strong rate sensitivity. This detailed analysis applied to the strain rate dependence will be discussed in a forthcoming paper.

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