

PROBE TACK INVESTIGATIONS OF POLY(VINYL PYRROLIDONE)-POLY(ETHYLENE GLYCOL) BLENDS

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INTRODUCTION

Pressure-sensitive adhesives (PSA) are commonly used in transdermal drug delivery systems where they both perform as adhesives and reservoirs. We studied biocompatible blends of glassy poly(vinyl pyrrolidone) (PVP) and liquid poly(ethylene glycol) (PEG) (Fig. 1).

Compatibility in PVP-PEG blends is provided by H-bonded interactions between PEG hydroxyl terminal groups and carbonyl groups of the monomeric units of PVP, and has been studied by Feldstein and al. [1]. As these blends are very hydrophilic, it has been reported [2] that their adhesive properties depend both on PEG content and water content. Peel tests have been performed on a wide range of PEG content and relative humidity (RH) of air surrounding the samples during their preparation. Only the blends in a very narrow window around 36 wt. % of PEG showed high adhesion. This adhesion was enhanced for RH = 50 to 65 %.

Mixing long chains of PVP (~9000 monomeric units) with short chains of PEG (~9 monomeric units) results in a soft material with both elastic and viscous properties necessary to PSAs. The parallel geometry provided by probe tack tests is optimal to study soft adhesives. The adhesive layer is submitted to a uniform distribution of stress and deformation. As shown Fig. 2, our apparatus allows both acquisition of stress vs. strain curves and observation of the debonding mechanisms occurring in the adhesive layer such as cavitation and fibrillation [3].

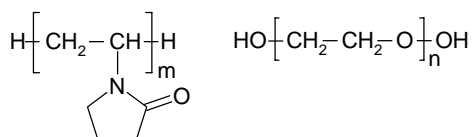


Fig. 1: PVP (left) and PEG (right)

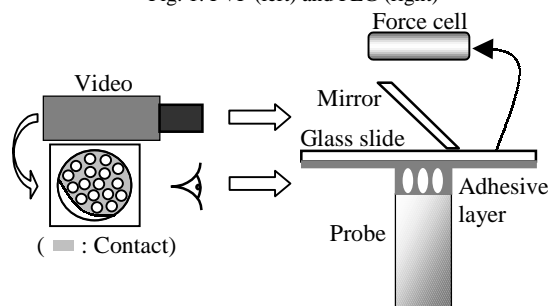


Fig. 2: Data acquisition and observation of micromechanisms in probe tack test experiment

We thus decided to study the influence of PEG content (around the optimal value found for peel tests) on the adhesive behaviour in probe tack as well as the influence of the debonding rate. DSC and rheological measurements were also performed in order to get complementary information on thermal and mechanical properties of the materials. These two last experimental results will be described in a forthcoming paper [4].

EXPERIMENTAL

MATERIALS AND SAMPLES PREPARATION

Poly (vinyl pyrrolidone), $M_w = 10^7 \text{ g.mol}^{-1}$ and poly (ethylene glycol), $M_w = 400 \text{ g.mol}^{-1}$ were obtained from *M.M. Feldstein*. Solutions in ethyl alcohol were prepared by dissolving both components during 12 hrs at room temperature. The PEG content varied from 31 to 41 %. Adhesive films (70 μm -thick) were then prepared by casting the solutions on microscope glass slides previously cleaned with ethyl alcohol. The films were dried first at room temperature during 24 hrs, then 2 hrs under vacuum, at 65°C. The water content of the adhesive films was finally equilibrated by leaving the samples at room temperature in desiccators under constant relative humidity (RH = 53 %) for 6 days. The water content was measured at 11 wt. % by weight loss under drying (vacuum, 90°C). This RH is provided by a sulfuric acid solution with $d = 1.29$.

PROBE TACK TEST EXPERIMENT

We performed probe tack tests on our custom-designed apparatus using a MTS 810 hydraulic testing machine previously described in [3]. One test is divided in three parts (Fig. 3). A flat stainless steel probe (diameter 10 mm) approaches the adhesive layer lying on a microscope glass slide at a constant velocity ($V_{APP} = 30 \mu\text{m.s}^{-1}$). When the contact pressure (P_C) reaches 1 MPa, the movement stops during a contact time (t_c) of 1s. The probe is then removed at a constant debonding velocity (V_{DEB}) varying from 1 to 80 $\mu\text{m.s}^{-1}$.

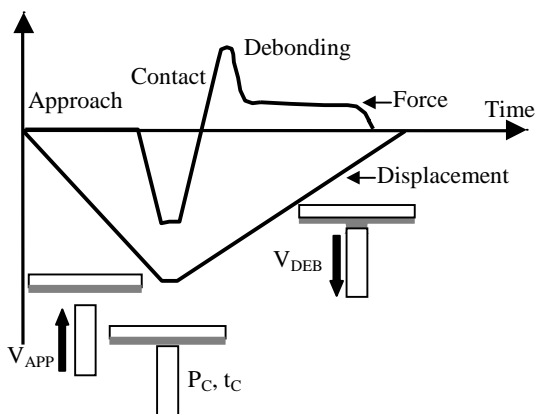


Fig. 3: Typical probe tack test

Force vs. time and displacement vs. time curves are thus directly obtained. Stress vs. strain curves are then calculated using the values of film thickness and measured contact area.

Adhesive films were mostly tested at room temperature (24°C) within 10 min after being taken out of conditioned dessiccators. No significant weight loss (i.e. water loss) was detected after probe tack tests.

We will be interested in the values of the maximum stress (σ_{\max}) as well as in the values of the maximum elongation at break (ϵ_{\max}) obtained during the test.

RESULTS AND DISCUSSION

We varied two parameters: PEG content (31, 36, 41 wt. %) and debonding velocity V_{DEB} (1, 2, 5, 10, 20, 50, 80 $\mu\text{m}\cdot\text{s}^{-1}$).

INFLUENCE OF PEG CONTENT

Fig. 4 shows representative stress vs. strain curves for the three PEG contents at $V_{\text{DEB}} = 5 \mu\text{m}\cdot\text{s}^{-1}$. One can see that an increase in PEG content leads to a decrease in maximal stress σ_{\max} and to a significant increase in maximal elongation ϵ_{\max} . These trends have been observed for all debonding velocities between 1 and 80 $\mu\text{m}\cdot\text{s}^{-1}$.

The 36 wt. % blend appears to be a good compromise for these two parameters. If there is more than 36 wt. % PEG, the blend is mainly viscous and the elasticity of the material is reduced but its ability to sustain high deformations is important. On the other hand, if there is less than 36 wt. % PEG, the blend is mainly elastic and adhesive films debond rapidly under low deformations.

The addition of small molecules of PEG (low T_g) leads to the same effects on σ_{\max} and ϵ_{\max} as do the addition of tackifying resins (high T_g) in styrene-isoprene-styrene block copolymers [5]. These small molecules reduce the glass transition temperature of the blend and therefore allow us to obtain a softer material at room temperature. The elastic modulus of materials containing more PEG will then be lower, leading directly to a lower σ_{\max} , and a higher ϵ_{\max} in probe tack test experiments.

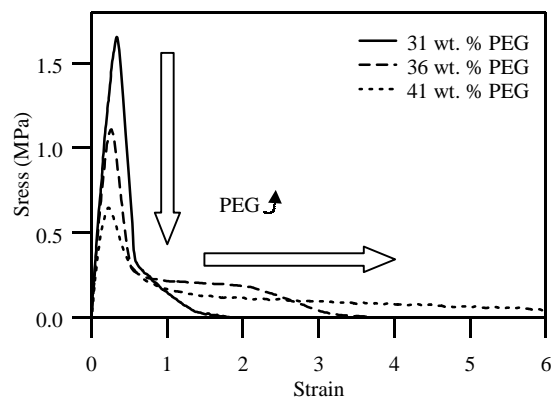


Fig. 4: Influence of PEG content under constant debonding velocity ($V_{\text{DEB}} = 5 \mu\text{m}\cdot\text{s}^{-1}$)

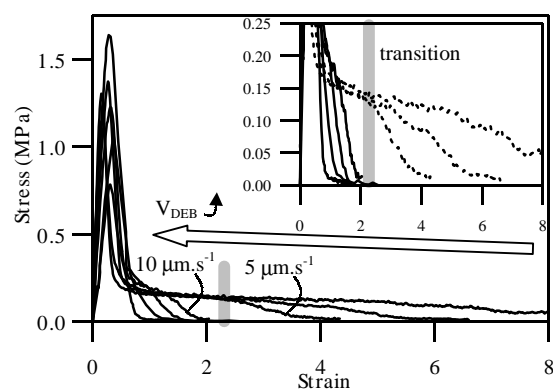


Fig. 5: Influence of debonding velocity at constant PEG content (36 wt. % PEG)

INFLUENCE OF DEBONDING VELOCITY

Fig. 5 shows representative stress vs. strain curves for the blend with 36 wt. % PEG: increasing the debonding velocity V_{DEB} has no obvious effect on σ_{\max} (Fig. 6) but leads to a significant decrease in maximal elongation ϵ_{\max} . The material response shows a transition at a given debonding velocity: at low debonding velocities (here $V_{\text{DEB}} \leq 5 \mu\text{m}\cdot\text{s}^{-1}$), stress vs. strain curves show a plateau before complete debonding, giving high values for ϵ_{\max} . On the contrary, at high debonding velocities, there is no plateau and the debonding occurs immediately.

The decoupling between σ_{\max} and ϵ_{\max} and the existence of a transition for ϵ_{\max} are two characteristics of PEG-PVP blends and have been observed for the three compositions as shown Fig. 6. The maximal elongation is only driven by the PEG content and the transition occurs at a higher debonding velocity if there is more PEG in the blend.

CONCLUSIONS

Tack properties of model water-soluble PSA based on poly(vinylpyrrolidone) and poly(ethylene glycol) have been investigated. At room temperature, two important effects are observed.

- 1) The adhesive properties are very sensitive to the amount of PEG in the blend in the range of 30-40%. At low PEG content no fibrillation is observed but σ_{\max} is high while at high PEG content, σ_{\max} is low but extensive fibrillation is observed.
- 2) For the blend containing 36%, a clear transition between a debonding without fibrils to a debonding with extensive fibril formation occurs at an intermediate velocity without any change in σ_{\max} . This result implies that an adhesive could be designed to have a high adhesion energy at low debonding rates but a good release at high debonding rates.

REFERENCES

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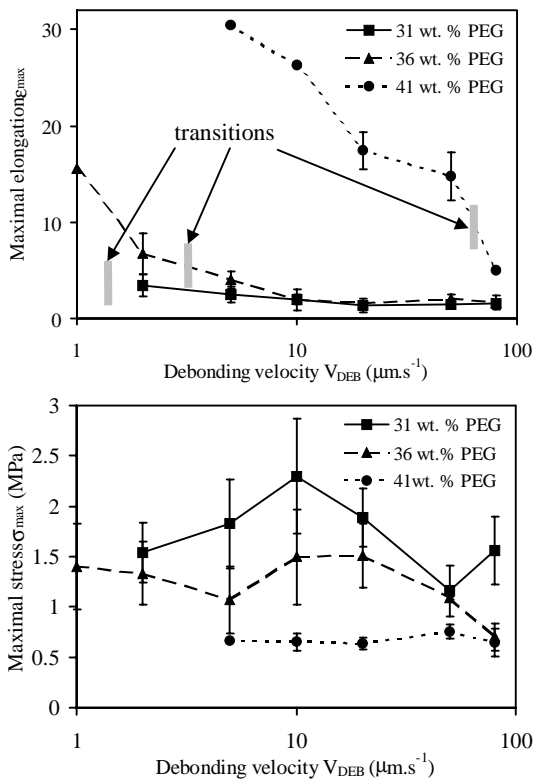


Fig. 6: Statistical results for σ_{\max} and ϵ_{\max} (PEG content = 31, 36, 41 wt. %, $V_{\text{DEB}} = 1$ to $80 \mu\text{m}\cdot\text{s}^{-1}$)

MICROMECHANISMS INVOLVED

Mechanisms involved in probe tack test experiments are commonly divided in five parts [3]: homogeneous deformation before σ_{\max} , cavitation around σ_{\max} , rapid growth of cavities during the steep decrease of σ , then, if there is a plateau, slow growth of these cavities and elongation of the walls in-between (fibrillation) and eventually, complete debonding.

PVP-PEG blends follow this general description and we only obtained adhesive debonding from the probe.

The observation of the debonding mechanisms provided additional information on the nature of the transition in ϵ_{\max} with debonding velocity. Images taken at a velocity lower and higher than the transition velocity showed that the adhesive responded overall in the same way until the complete formation of the cavities (same σ_{\max} and $\epsilon \leq 1.5$). Then, the adhesive showed a yield behaviour which was strongly dependent on the velocity: at low velocity, a yield process occurred and the chains became oriented to form fibrils (plateau); at high velocity, debonding occurred by coalescence of the cavities without any fibrillation. This decoupling between cavitation and fibrillation is not inconsistent since we consider two mechanisms which require a different type of deformation (shear / elongation, small deformations / large deformations), and occur at different strain rates.