

ADHESION AND DEFORMATION OF HETEROGENEOUSLY CROSSLINKED WATERBORNE PRESSURE SENSITIVE ADHESIVES

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Introduction

The properties of PSA are industrially evaluated with a shear test, testing the cohesion of the material and a peel test, testing its detachment force under standardized conditions. Optimization of a PSA for a specific application requires a balance between these two properties.

We report here some results on a new generation of waterborne PSA resulting from the coalescence between latex particles. The well documented complexity^{1,2} of the molecular structure of the polymers in the particles and the near impossibility to have an independent control of the monomer composition and molecular weight distribution and gel fraction, has led us to study so-called core-shell particles³. We targeted structures where the dissipative viscoelastic properties necessary to obtain a high peel force are mainly controlled by the structure of the core, while the creation of covalent bonds between the shells imparts cohesion. (Figures 1 et 2).

Experimental

The Probe Tack tests have been carried out at room temperature on a custom-designed tester⁴ with the following parameters: approach velocity : $V_{app} = 30 \mu\text{m}\cdot\text{s}^{-1}$, contact force $F_c = -70 \text{ N}$, contact time : $t_c = 1\text{s}$, debonding velocity : $V_{deb} = 10 \text{ à } 1000 \mu\text{m}\cdot\text{s}^{-1}$. The PSA films are prepared by doctor blading the emulsion on a glass slide and dried about 10 hours at room temperature and 5 minutes at 110°C . the dry thickness is close to $100 \mu\text{m}$.

The small strain viscoelastic properties have been obtained with a custom designed micro rheometer. The storage and loss modulus, at a frequency ranging between 0.1 and 10 Hz, have been calculated from the measured contact stiffness of a sapphire sphere with the adhesive film⁵.

The tensile tests have been carried out on a standard tensile tester equipped with a non contact extensometer. The films, $800 \mu\text{m}$ thick were tested at room temperature at an initial strain rate of 0.05 s^{-1} .

The materials have been synthesized by emulsion polymerization in starved conditions. The synthesis is done in two stages, first the core, then the shell ($\varnothing_{total} = 250 \text{ nm}$). The monomer composition is typical of acrylic PSA giving a low T_g polymer, identical for the core and the shell. In addition a small and controlled amount of diacetone acrylamide (DAAM) is added in the shell. It is the reaction of these groups with adipic acid hydrazide molecules dissolved in the aqueous phase during the drying step, that leads to the interparticle crosslinking imparting the cohesion to the PSA film (Figures 1 et 2). The crosslinking density depends on the thickness of the shell and the density of reactive groups contained therein. The percentage of crosslinking referred to as X is defined as the ratio between the actual amount of ADH added and the stoichiometric amount necessary to fully react with the DAAM groups.

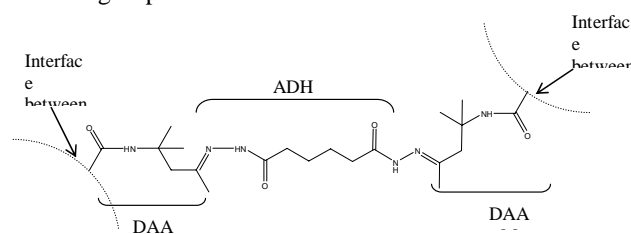


Figure 1: Covalent bonds connecting two DAAM groups at the surface of two particles. They are created during drying after adding ADH molecules to the latex

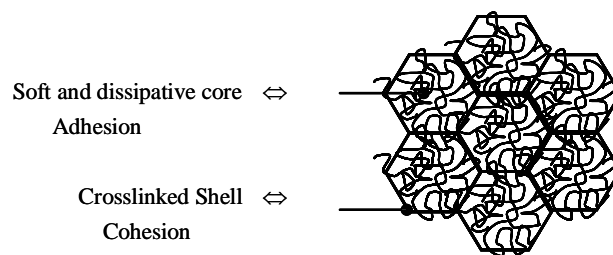


Figure 2: Honeycomb structure of the dry film This structure is predicted after drying of the particles (deformation and coalescence).

Results and Discussion

Activation of crosslinking

The first measurements have been carried out on thin shell (around 9 nm) materials. The crosslinking density X is controlled by the amount of ADH added to the aqueous phase.

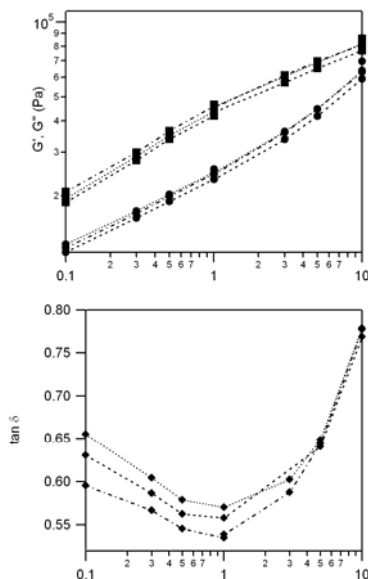


Figure 3. Left : Evolution of the elastic (G' , ■) and loss moduli (G'' , ●) as a function of frequency. Right : Evolution of $\tan \delta = G''/G'$ as a function of frequency. (..... : $X=23\%$, - - - : $X=59\%$ et - . - . : $X=110\%$).

The results show that the linear viscoelastic properties are not very affected by the interfacial crosslinking (Figure 3). No obvious evolution of the elastic and viscous moduli as a function of crosslinking density is visible except for a small decrease in $\tan \delta$ at low frequency for increasing crosslinking density.

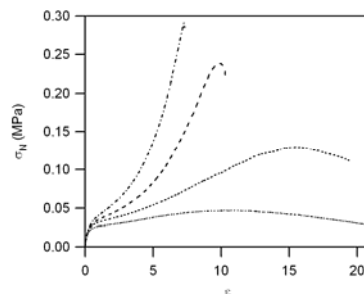
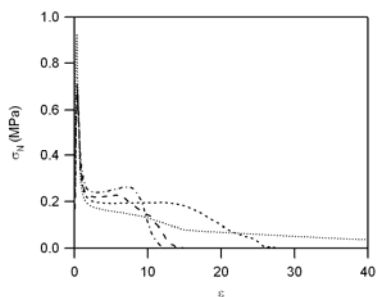


Figure 4. Large strain properties of the core-shell PSA as a function of crosslinking density. Left : probe tack curves on steel, $V_{dec} = 100 \mu\text{m}\cdot\text{s}^{-1}$. Right : tensile testing curves. (..... : $X=0\%$, : $X=50\%$, - - - : $X=75\%$ et - . - . : $X=100\%$).

At large strains, the effect of an interparticle crosslinking is remarkable (Figure 4). An increase in crosslinking density leads to a progressive increase in the strength of the material.; a transition from a liquid-like flowing and yielding behaviour to a solid-like rubbery behaviour is clearly observable in the tensile tests. In the adhesive tests, the uncrosslinked samples fails cohesively (with residues on the probe) while the crosslinked samples detach cleanly from the probe.

Influence of the localisation of crosslinking points

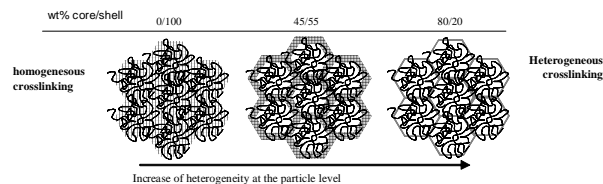
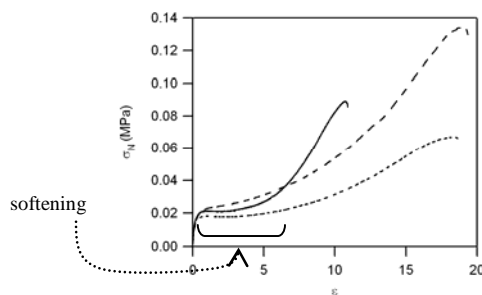


Figure 5. Schematic representation of the structure of dry films prepared from particles with a different spatial distribution of DAAM groups.



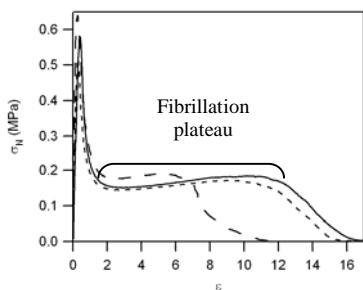


Figure 6. Stress-Strain curves. Left : tensile results. Right : tack results on steel at $10 \mu\text{m}\cdot\text{s}^{-1}$. wt% core/shell : - - - 0/10,45/55 and ——— 80/20.

The spatial distribution of crosslinking points (Figure 5) has the most influence at intermediate and large strains (Figure 6). In this regime the materials soften markedly and this softening is necessary to form the fibrillar structure by avoiding interfacial crack propagation.

The tack results of Figure 6 show that the debonding occurs at higher extensions for the heterogeneously crosslinked particles. Since the detachment of the fibrils is controlled by a balance between the energy that can be released by the extended fibrils and the energy necessary to detach the foot of the fibril. A more dissipative material with only a slight decrease in cohesion will have a higher adhesion energy.

In the case of the 80/20 material, the crosslinking point at the edge of the particles does not influence much the behaviour of the core which remains very viscoelastic and dissipative. On the other hand, the homogeneously crosslinked particle is more elastic and this lower level of viscoelasticity, which is more apparent at intermediate strains, causes an early detachment of the probe.

These results have been further confirmed by standard PSA tests performed on the same materials and showing that the interfacial crosslinking localized in the shell is a very effective way to provide a percolating network of crosslinks, able to cause strain hardening in the material without much loss in dissipative properties.

Conclusions

The interfacial crosslinking of latex particles during drying is a very good strategy to impart cohesion to a waterborne PSA without decreasing too much the dissipative properties. This enhances significantly the shear resistance of the PSA without detrimentally affecting the peel force.

References

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