

WATER BASED PRESSURE SENSITIVE ADHESIVES WITH ENHANCED WATER RESISTANCE FOR CLOSING THE GAP WITH SOLVENT BASED PRODUCTS

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INTRODUCTION

After a brief introduction, we describe some phenomena that, properly exploited, can allow to increase further the peel adhesion. They are taken from the scientific literature and exploit the following concepts:

- 1) Morphology of the polymeric network (polymer chains)
- 2) Energy dissipation
- 3) Morphology of the latex particles
- 4) Morphology of the adhesive film

Of course these concepts have been already exploited, even if implicitly; however full awareness has led and will lead to further improvements. Then we report some examples, taken from literature, of acrylic PSAs with high peel adhesion and reasonable shear resistance. We mention, very shortly, the underlying phenomena responsible for that.

In the second part we discuss the effect of water on PSAs and the strategies to improve water resistance

1. High-peel pressure sensitive adhesives.

Looking at the real peeling (picture) we can represent it with a mathematic model, tensile tests on a PSA polymeric film can be used as a criterion for extrapolating values of peel adhesion for the adhesive itself. Tensile tests correlate well with the structure of the polymer; moreover in the scientific literature is easier to find data about tensile tests than peel tests.

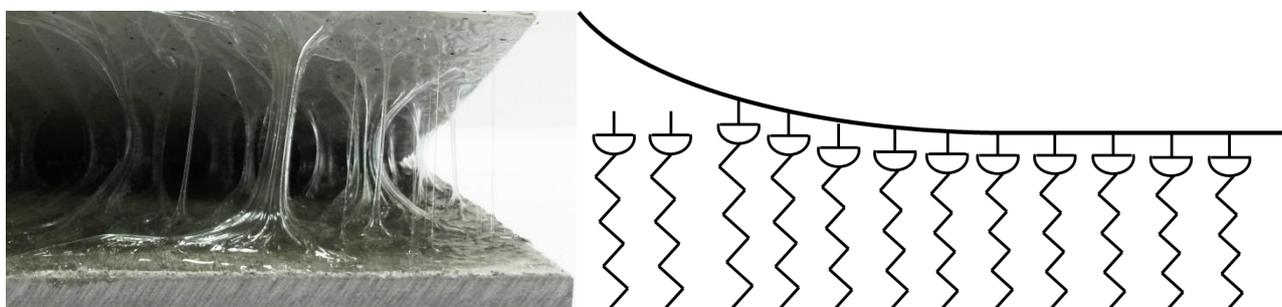


Figure 1

When peeling a pressure sensitive adhesive, formation of fibrils takes place. Considering the fibrils (**Figure 1**), in a tensile test the work expended till failure is:

$$W_{tot} = W_{ad} + W_{el} + W_d,$$

where W_{ad} is the energy of adhesion (very small so we neglect its contribution), W_{el} is the elastic deformation energy and W_d is the energy dissipated (viscous component). In this context we consider only contributions from the mass of the adhesive, not those coming from the carrier, even if they can be important.

If we look at a tensile test on single fibrils ⁽¹⁾ the energy required to destroy the bond is given by the area of the stress-elongation until failure.

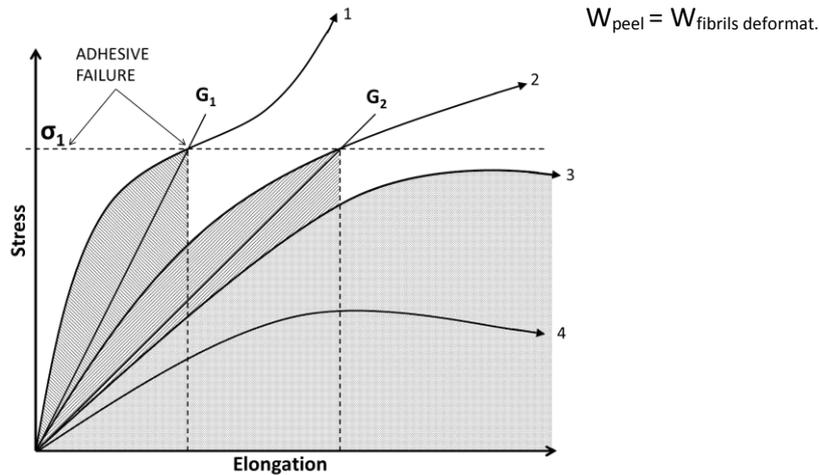


Figure 2

The symbol σ_0 in the curve corresponds to the stress necessary for interfacial debonding. In case of adhesive failure the area to be considered is under the intercept stress-strain curve and σ_0 . If the stress-strain curve does not intercept σ_0 the result is cohesive failure. Looked from this point of view, the interfacial energy of adhesion is not important *per se*, but because it determines the level of the intercept between the stress-strain curve and σ_0 and consequently the area (energy) subtended. Of course if we consider the test on a polymer specimen, it has to be done at the same deformation rate we have on the fibrils in a peel test.

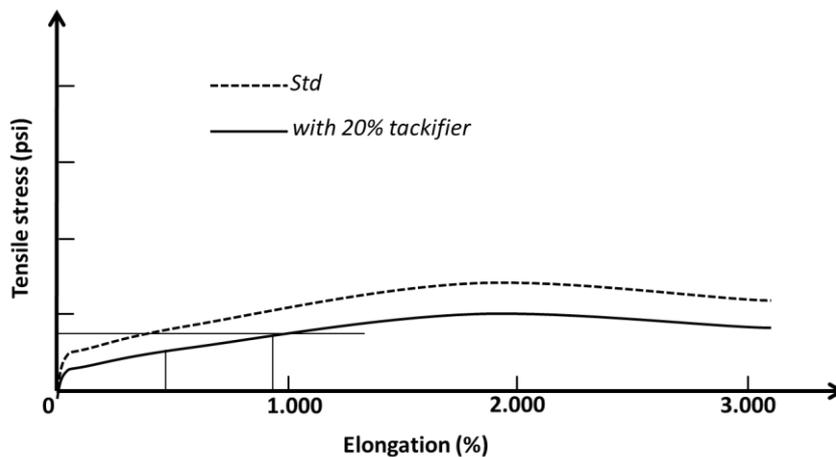


Figure 3

In the figure ⁽²⁾ it is shown a tackified adhesive vs. an untackified, the tougher material will show a lower peel adhesion. This is clear if we look at the intercept between the stress-strain curves and σ_0 (horizontal line) and consequently the area subtended (energy to rupture).

The same applies if we consider a crosslinked polymers vs. an uncrosslinked one ⁽³⁾

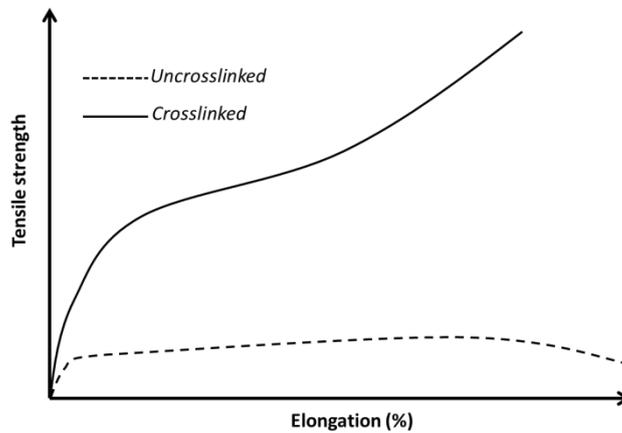


Figure 4

2. Polymer network morphology

Now we look at different mechanisms which can be exploited to have a more favorable stress-strain behavior and consequently higher peel adhesion for PSAs. The first mechanism we consider is related to the morphology of the polymer network, in other words the spatial distribution of polymer chains and crosslinks.

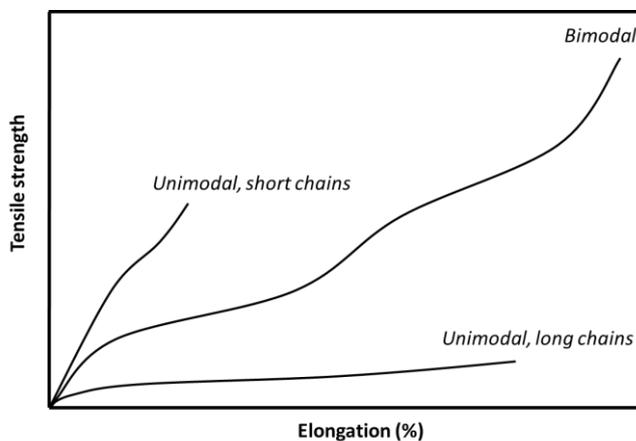


Figure 5

Elastomers are slightly crosslinked, soft polymers. The Figure 5 ⁽⁴⁾ shows stress-strain curves for a unimodal highly crosslinked, a unimodal lightly crosslinked and a bimodal crosslinked elastomer. We see that the latter is much tougher compared to the other two. By just changing the mode of crosslinking there corresponds a big variation in the energy absorbed to failure.

Let us look a similar phenomenon in a different field, hydrogels ⁽⁵⁾. Here we have three different systems:

- a) an alginate, with ionic crosslinks through Ca^{2+} ions;

- b) a polyacrylamide gel crosslinked through covalent bonds (N,N-methylenebisacrylamide);
- c) a “mixture” of the two where we see that this system is orders of magnitude tougher than the “pure” polymers.

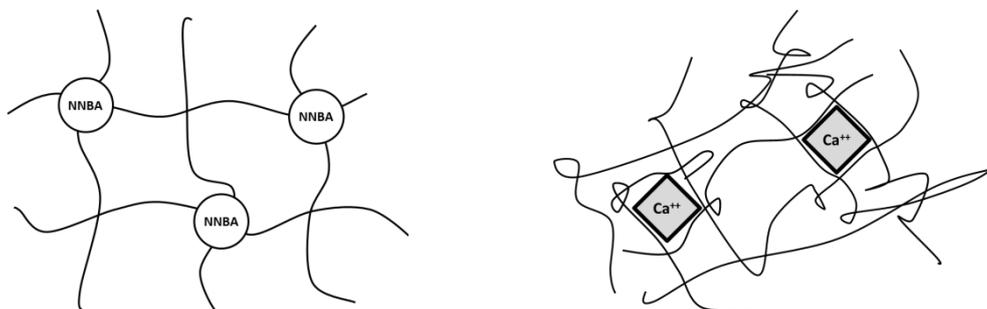


Figure 6

The energy absorbed till failure is orders of magnitude larger. This is mainly (even if not only) achieved by the use of distinct crosslinking mechanisms in the formulation.

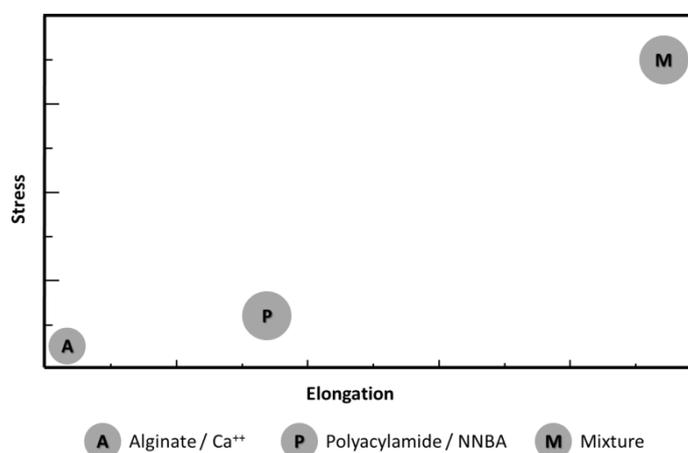


Figure 7

3. Energy dissipation

The next mechanism we must consider concerns energy dissipation, sometimes reported as “viscous flow” and related to friction forces. The larger the interactions between polymer chains, the higher the energy dissipated when they are deformed, the next system described is composed by three polymers ⁽⁶⁾: polyvinylpyrrolidone (PVP), polyethylene glycol (PEG) and polyacrylic acid (PAA) . Both PAA and PVP are hard polymers at room temperature and the function of PEG, which is compatible with both polymers, is to lower the glass transition temperature of the system, well below room temperature. We could have a pressure sensitive adhesive also with PAA and PEG or PVP and PEG, but with poor characteristics, unless covalently crosslinked. Having a system with the three components allows for strong complementary hydrogen bonding interactions, which are destroyed and continuously reformed during deformation as shown in Figure 8.

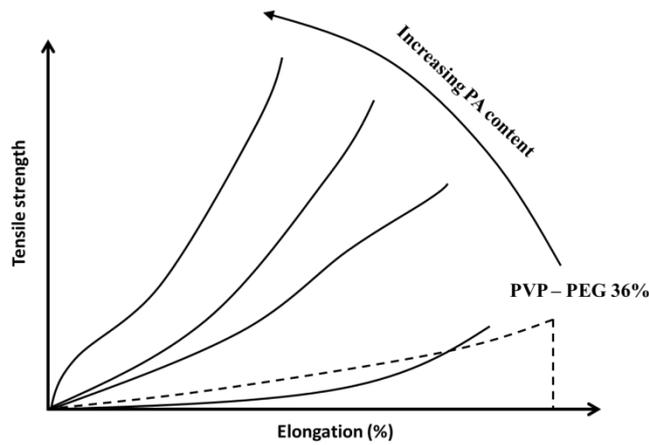


Figure 8 - Tensile properties of PVP-PEG-PAA in function of PAA

The chemical-physical behavior is well illustrated in the stress-elongation diagram of Figure 9. Under deformation hydrogen bonds between PAA and PVP-PEG are destroyed but they continuously reformed, the consequence is continuous energy dissipation, resulting in higher Peel force.

Another effect given by Energy Dissipation is displayed in the next example ⁽⁷⁾, a Polybutylacrylate polymers (PBA) were synthesized with different bearing functional groups:

- acrylic acid
- Vinylpyrrolidone
- Tyrosine
- Adenine

While the former two can only form hydrogen bonding the latter two can form multiple noncovalent interaction, as shown in Figure 8.

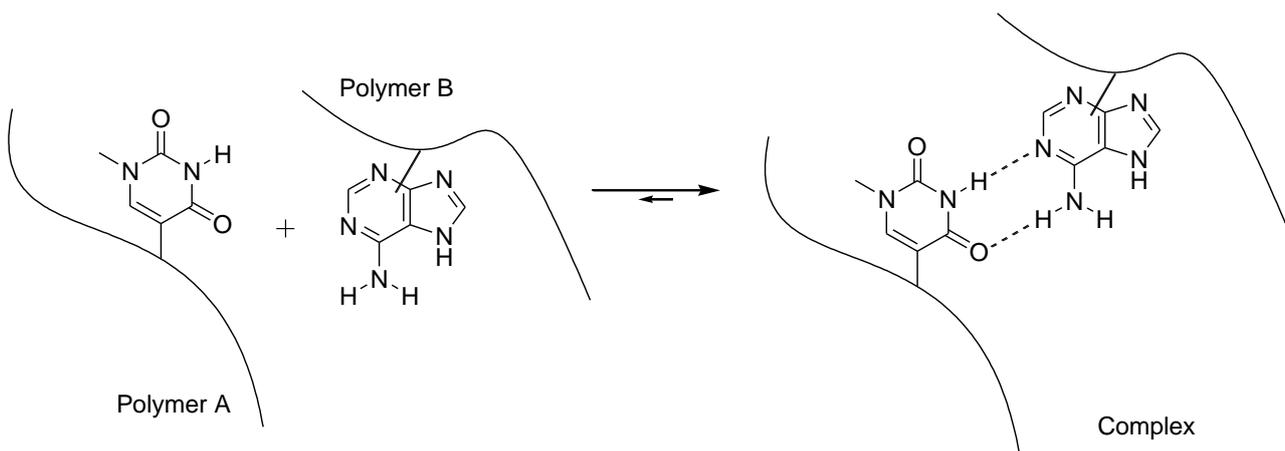


Figure 9

The effect on both Peel Adhesion and Shear Strength is evident, the blends of polymers

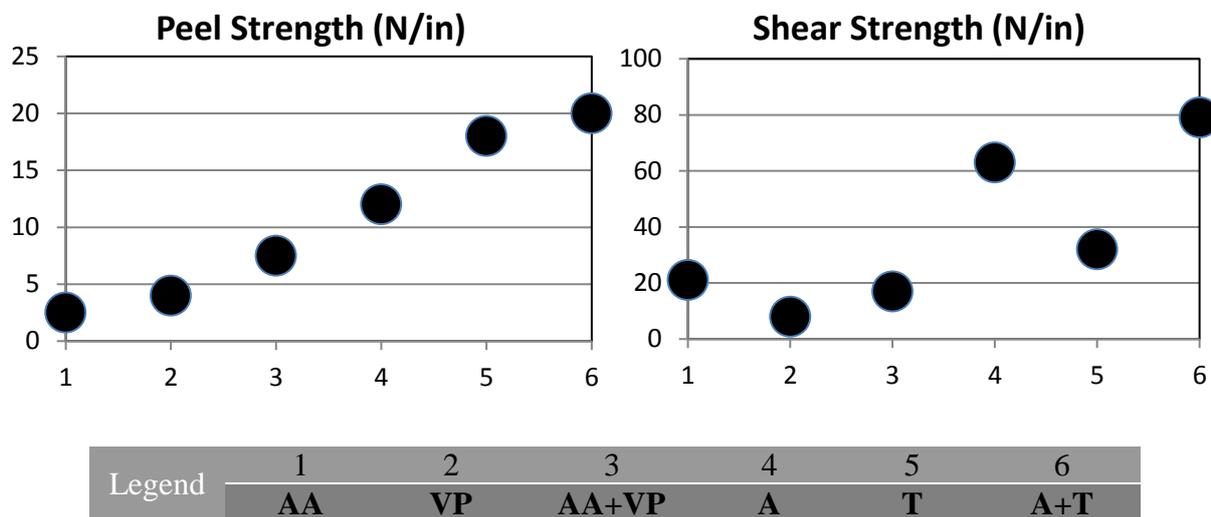


Figure 10

Effect of complementary hydrogen bond interactions on Peel and Shear

T = Tyrosine – A = Adenine

If we blend only the polymers with acrylic acid and vinylpyrrolidone (acid base interaction) you see a moderate increase of Peel Force and negligible effect on Shear, while including the two polymers bearing Tyrosine and Adenine the blend shows definitely superior performances both in Peel Adhesion than in Shear Strength (see Figure 9).

4. Particles Morphology

The next aspect to consider is the influence of Latex Particles Morphology on the performances of P.S.A., this aspect is crucial, often there is the assumption that after film formation of a water based polymer dispersion a uniform film is obtained.

This is more an exception than a rule, even with very low Glass Transition (T_g) Temperatures as in the case of acrylic pressure sensitive adhesives, the particles will maintain some identity after film formation, during polymerization crosslinking *in* the particles takes place, due to chain transfer, and this will remain after film formation, this is valid both in case when we purposely build structured particles like core-shell or inclusions and when the polymerization is homogeneously carried on.

Pressure sensitive adhesives were synthesized in two stages⁽⁸⁾, obtaining core/shell particles. During the polymerization of the shell a small amount of diacetone acrylamide (DAAM) was added. At the end adipic acid hydrazide (ADH) was added, in different amounts. During the drying stage the reaction between DAAM groups and ADH leads to interparticle (interfacial) crosslinking, imparting cohesion to the PSA. 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.

An increase in crosslinking density leads to a progressive increase in the strength of the material: a transition from a liquid-like flowing behavior to a solid-like rubbery behavior 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.

Tests were also made by crosslinking the core: a substantial decrease of adhesion was observed. The conclusion was that 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 of the core. This enhances significantly the shear resistance of the PSA without detrimentally affecting the peel force, see Figure 9 : crosslinking (and its distribution) in latex particles.

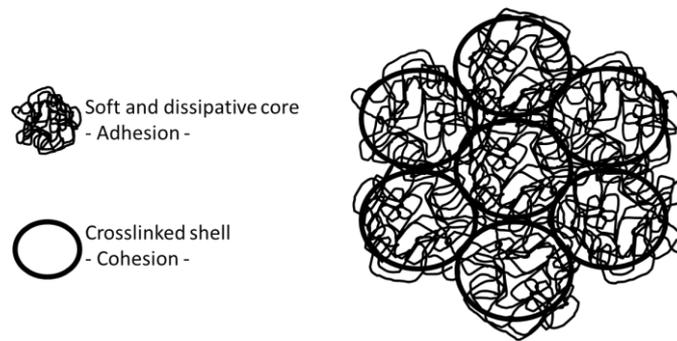


Figure 11

In the honeycomb structure of the dry film, the dissipative viscoelastic properties necessary to obtain high Peel force are mainly controlled by the structure of the core, while the creation of covalent bonds between the shells impart cohesion (Shear).

A completely different strategy ⁽⁹⁾ can be chosen for obtaining a very highly adhesive P.S.A.: a two-stage polymerization process can be adopted. The first stage being conventional, a semi batch polymerization, the second stage is a swelling polymerization, to the polymer of the first stage is added a monomer (in relatively small amount, say 5%) corresponding to a high T_g polymer. After the addition a second polymerization stage took place. The films obtained from these latexes are showing both higher peel adhesion and shear resistance.

Transmission electron micrographs of the films showed that inside the latex particles nanoparticles were formed. But these did not act as ordinary fillers. It could be argued that the second stage increases crosslinking by chain transfer, but this would increase cohesion as well, but at the expense of peel adhesion. A straightforward explanation does not exist at the moment. We believe that it will come from a deeper investigation at the nanoscale, anyway the results obtained are quite impressive:

Table 1 Adhesive properties before and after second stage of swelling polymerization

Latex	Quick stick	180°Peel Adhesion (N)	500g Shear Adhesion
FIRST STAGE	10,7	6,8	246 min
SCOND STAGE	10,3	13,7	➤ 24 hours

Table 1

Considering morphology of latex polymers in crosslinked and uncrosslinked particles⁽¹⁰⁾ we can take in consideration three important parameters:

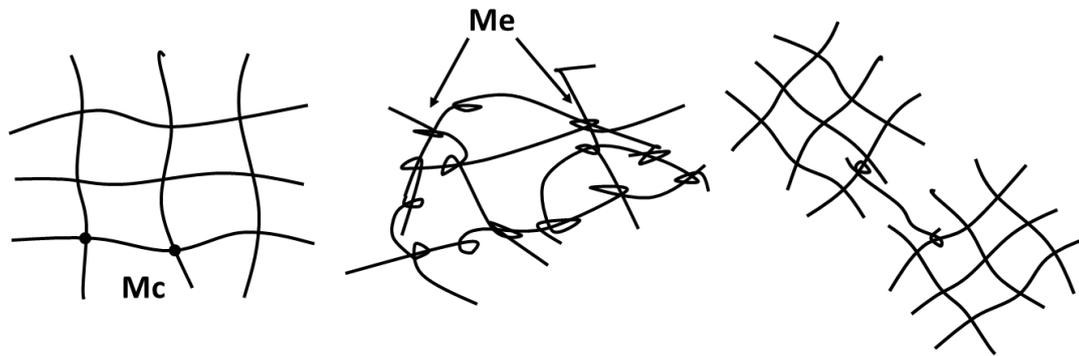


Figure 12

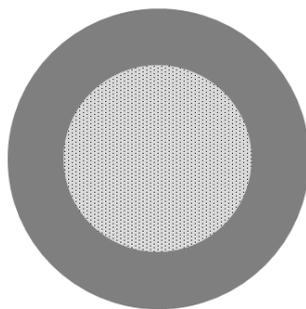
- “ M_c ” that indicates the average molecular weight between crosslinking points: In a latex we almost have a “gel fraction”, formed by intentional crosslinking of by chain transfer
- “ M_w ” is the average molecular weight of the uncrosslinked polymer
- “ M_e ” is the average molecular weight between entanglements in a linear polymer. Its value is peculiar of each polymer and depends on its composition. For acrylic polymers it is related mainly to the steric hindrance of side groups (with bulky side groups the molecular weight between entanglements will be higher).

Incidentally, M_e is related to the modulus of the polymer above T_g , the higher it is, the lower the modulus and higher tendency to form fibrils during peeling. Therefore, it is preferable to have higher M_e .

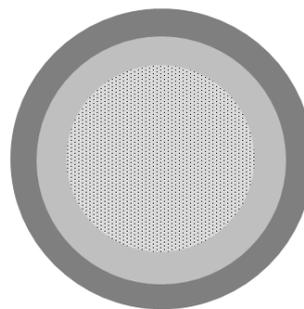
Mixing latexes with crosslinked particles and others which are totally uncrosslinked, the best P.S.A. performances are attained when $M_c > M_e$ and $M_w > 2M_e$. the latter condition is necessary for the linear uncrosslinked polymer to penetrate inside the crosslinks of the other polymer and connect together two crosslinked entities by entanglement.

- Structured particles with two and three layer⁽¹¹⁾.

Two-layer particle



Three-layer particle



- ▨ Core copolymer (no crosslinking groups contained)
- ▨ Interlayer copolymer (crosslinking during polymerisation using HDDA)
- ▨ Shell copolymer (containing crosslinkable functional groups from DAAM)

Figure 13

The three layer particle had a core, a shell and an interlayer. The interlayer was crosslinked during polymerization with hexanediol diacrylate (HDDA), a bifunctional monomer. The shell was made crosslinkable with the system DAAM/ADH, yielding interparticle crosslinking.

The two layer particles were just lacking the interlayer. Dodecylmercaptan (DDM), a chain transfer agent, was adjusted in both the core and the shell.

The best results were achieved without interlayer, a Peel Adhesion > 20 N/in was reached with acceptable shear resistance, the amount of chain transfer was adjusted in the core and in the shell.

This study confirms the importance of a viscoelastic component coupled with interfacial crosslinking, obtainable with structured particles.

Morphology of the adhesive layer

In a polymer layer ⁽¹²⁾, stiff fibers can be introduced, the elastic “roughness” enhances the adhesion for a smooth interface and in this case, the adhesion energy can be amplified by a factor up to 100 times.

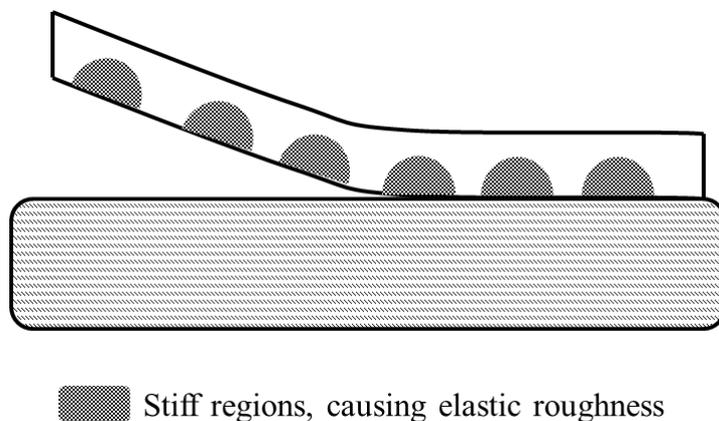


Figure 14

5. Effect of water on WB-PSAs.

When a pressure sensitive adhesive comes in contact with water or saturated water vapour, three main phenomena are observed:

- water whitening
- loss of adhesion and cohesion
- swelling.

To understand what happens, not only the composition of the dried polymeric film is important, but, even more, its morphology.

- 5.1 Water whitening

In a latex we find: surfactants, soluble oligomers, salts, additives and polymer particles. The polymer particles are surrounded by a hydrophilic membrane, which structure can be designed thanks to the polymerization process. In the film formed after the drying process the latex particles do not lose completely their individuality. Sometimes their structure is almost totally preserved.

After film formation and contact with water the following phenomena may happen:

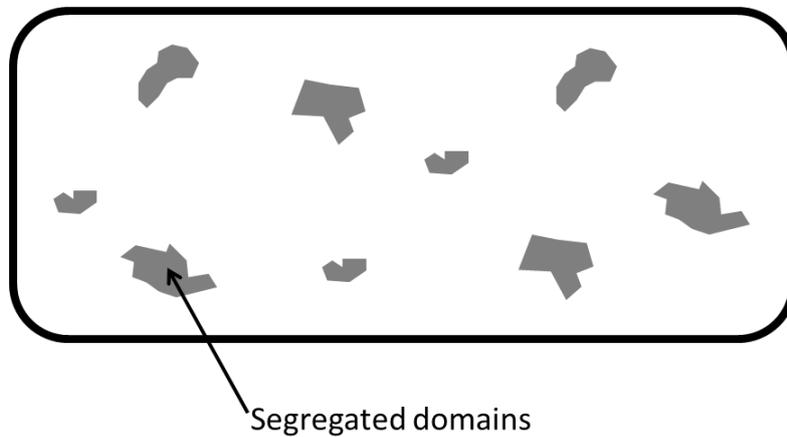


Figure 15

This segregation is producing water whitening. There must be present hydrophilic components (surfactants, oligomers, salts), not compatible with the polymer, which separate as a distinct phase. By immersion in water they absorb water by osmosis, increasing their size (comparable to the wavelength of visible light) and with a refractive index different from the main polymer phase. Consequently they will scatter light.

Counteracting actions:

- 1) minimizing the hydrophilic components
- 2) Interfacial crosslinking may help
- 3) Intra-particle crosslinking usually is detrimental.

- 5.2 Loss of adhesion and migration at interfaces

Surfactant and other compounds not compatible with the polymer, can migrate at the film/air and the film/substrate interfaces, after contact with water the consequence is loss of adhesion and blistering⁽¹³⁾, due to migration to the interfaces and building in this way a weak boundary layer.

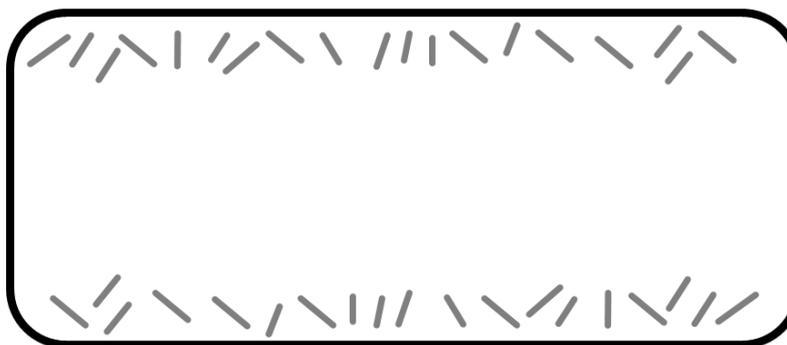


Figure 16

- 5.3 Swelling

A polymer film containing polar groups absorbs water and swells, the consequence is a worsening of mechanical properties.

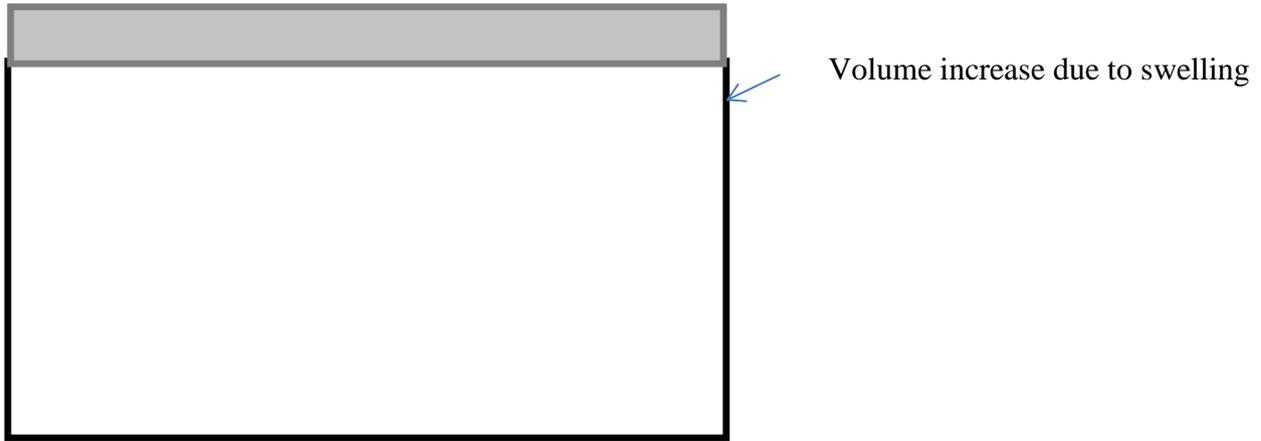


Figure 17

Water acts as a plasticizer for the adhesive, in some particular cases⁽¹⁴⁾ an increase of Peel Adhesion may be observed in the first contact with water.

Moisture can concentrate at the substrate/adhesive interface⁽¹⁵⁾, the consequence is a weakening of interfacial forces eventually combined with swelling and thus loss of adhesion.

- 5.4 Effect of particle with thick or stable membranes

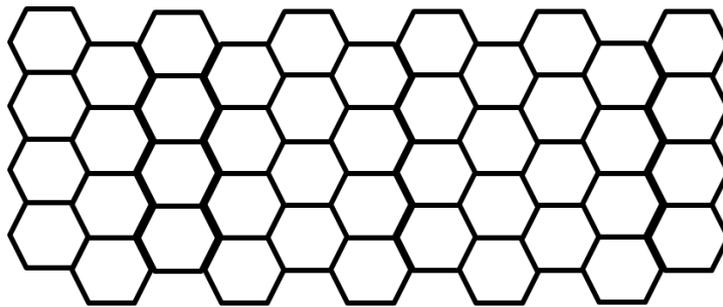


Figure 18

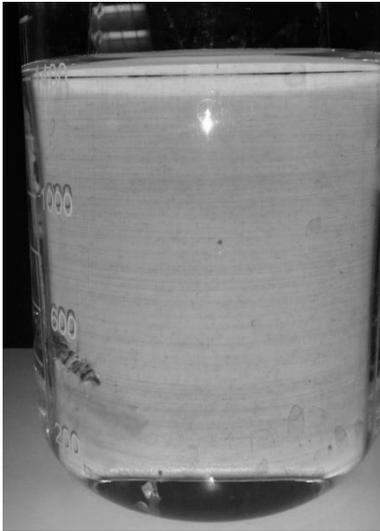
Particles with thick or stable membranes are considered⁽¹⁶⁾, this structure can be observed in the following cases: thick hydrophilic membranes, core-shell particles, crosslinked particles. Water can penetrate among the membranes and reduce the particle-particle and particle/substrate adhesion. Intraparticle crosslinking emphasizes the phenomenon, while interfacial crosslinking reduces it.

- 5.6 Synthesis strategies to obtain high water resistance and how to avoid the negative effects of water on the pressure sensitive ^{(17) (18)(19) (20)}
 - 1) Reduce the amount of water soluble and highly polar compounds
 - 2) Use non migrating surfactants (surfmers, polymeric surfactants)
 - 3) Avoid intraparticle crosslinking, exploit interfacial crosslinking
 - 4) Tailor the polarity of the adhesive
 - 5) Exploit interactions between surfaces and molecules that cannot be destroyed by water molecules, e.g. complementary hydrogen bonding
 - 6) Conduct nucleation polymerization and film formation at low pH

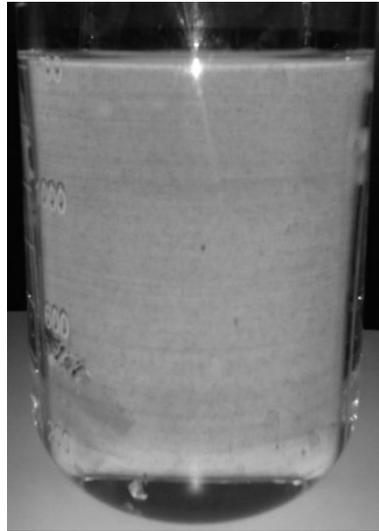
6. Experimental trials

Following the synthesis strategies described, some experimental polymerization have been performed and some test have been developed to measure the water resistance of the experimental product compared to product found on the market.

- 6.1 Immersion of film coated with 20 gsm of PSA on PET 26 micron film



**Figure 19 – Market product
AFTER 1h**



**Figure 20 – Market product
AFTER 4h**



**Figure 21 – Market product
AFTER 24h**



**Figure 22 – Experimental
ADH6 – AFTER 1h**



**Figure 23 – Experimental
ADH6 – AFTER 4h**



**Figure 24 – Experimental
ADH6 – AFTER 24h**

In these pictures it is clearly visible the difference of well-designed water resistance polymer in comparison with standard one

- 6.2 Rubbing of film after immersion, after the immersion seen in the previous test the film, just after removal from the water bath, is rubbed with a finger to test roughly the residual consistence

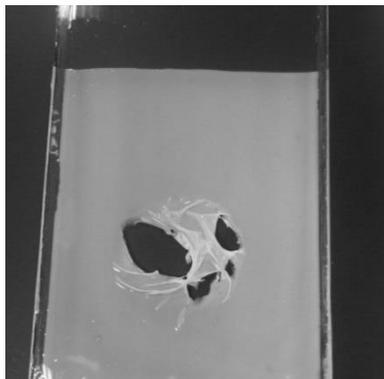


Figure 25 – Example of non-resistant film

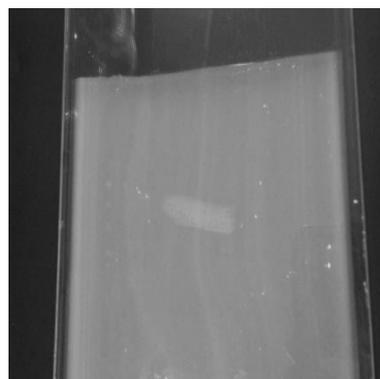


Figure 26 – Experimental ADH 6

The test is very simple but it shows the real strength the polymer retains after long contact with water

- 6.3 Haze measurement with Minolta CM-5 Spectrophotometer , measure are taken from the immersed and not immersed polymer, in order to have a numbered rating

	HAZE
Market Product	5,68
Experimental ADH 6	1,04

Table 2 – HAZE measurement

- 6.4 Contact Angle of water on the PSA film surface.

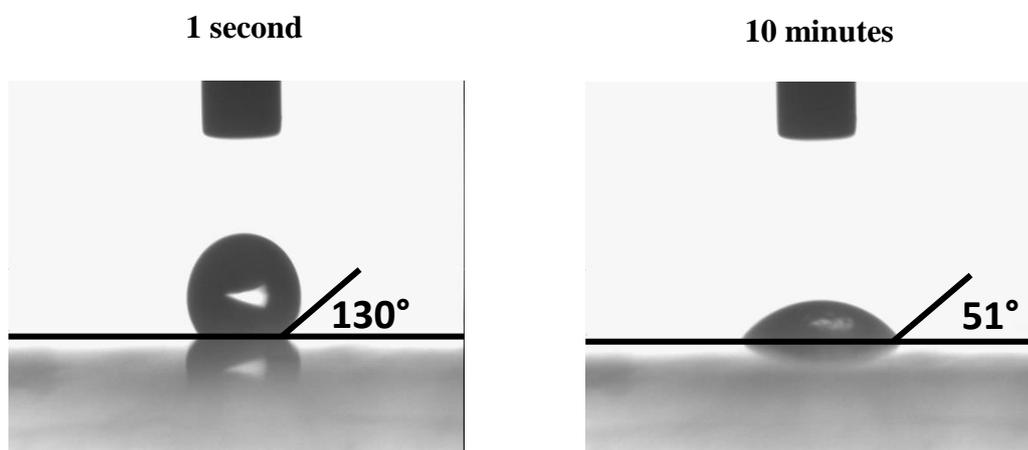


Figure 28 – Market product

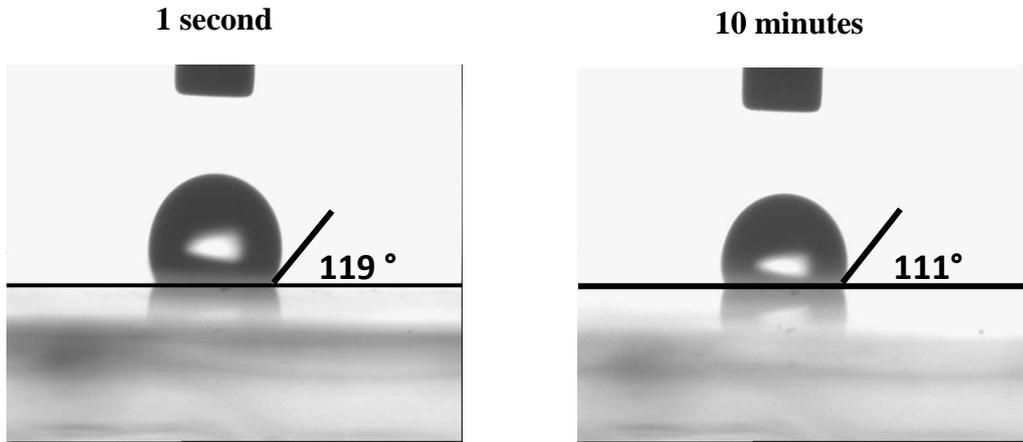


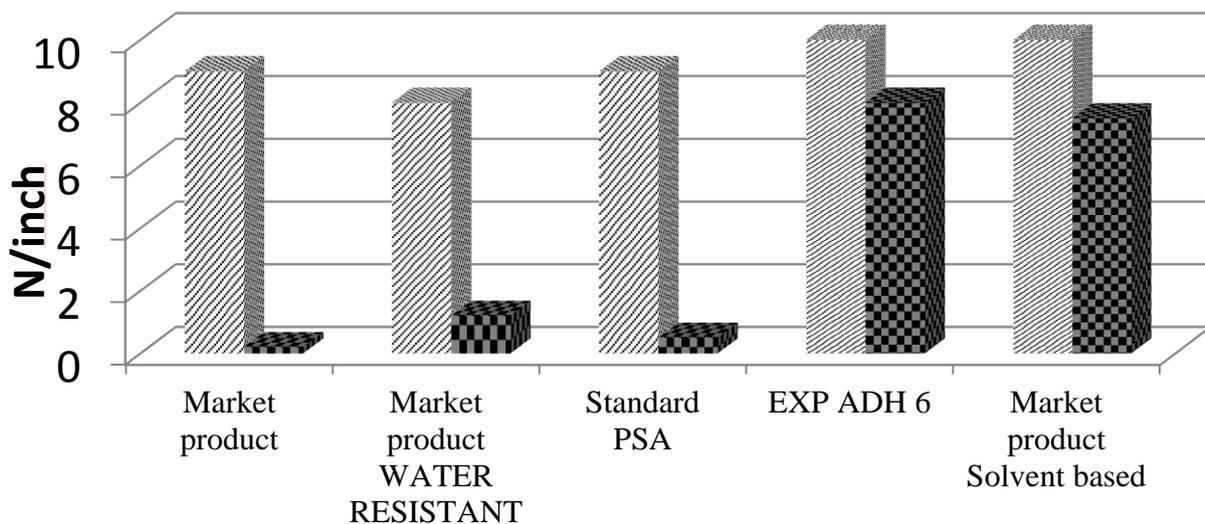
Figure 29 – Experimental ADH 6

- Peel testing

Another instrumental way of assessing the water resistance is done in this way:

The polymer is drawn down on PET 36 micron film at 20 gsm, it is dried in an oven at 80° for 5 minutes, then the sheet is cut in 1 inch width stripes and applied on glass test plates, half of them are conditioned at 23°C and 50 % r.h. and the other half are immersed in a beaker full of water and kept immersed for 24 hours at 23 °C. Then it is taken out and 180° Peel Adhesion is measured in comparison with the specimens not immersed in water.

In this Figure we see the results, before and after immersion, in the case of optimized water resistant polymer the values obtained are far greater than standard polymers and very near to a solvent based PSA taken from the market.



▨ FTM 1 on glass plate standard conditions

▣ FTM 1 after 24 hours of immersion in water at 23°C (dwell time out of the water 1 min)

7. Conclusions

A full review of literature regarding PSA behavior and properties has been made with the aim of finding the critical parameters to be taken in consideration for enhancing Peel strength and Cohesion of water based dispersion polymers, special care has been put to find the mechanism by which the water affects these polymers.

A series of techniques have been developed for underlining the effect of water on the polymers and trying to define some strategies for improving water resistance of PSA with the final aim of closing the gap between the water based polymer and the solvent based ones.

The results shown are very promising and let us think that this task is definitely possible.

8. Acknowledgment

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