DESIGN OF POLYURETHANE-ACRYLIC PRESSURE SENSITIVE ADHESIVES

Costantino Creton[1], Elise Degrandi[1], Ravidra Udagama[2], Elodie Bourgeat-Lami[2], Tim Mc Kenna[2]

[1]Laboratoire de Physico-Chimie des Polymères et Milieux Dispersés, CNRS-UPMC-ESPCI Paristech, Paris, France

[2]Laboratoire de Chimie et Procédés de Polymérisation, CNRS-CPE Lyon, Villeurbanne Cedex, France

Introduction

Environmental concerns stimulate the development of products coming from a sustainable technology. This leads to an increased use of waterborne products, and new synthesis methods have been developed. Although it is not yet widespread in industry, miniemulsion polymerization allows the incorporation of a hydrophobic second phase in droplets of monomer in order to obtain, after polymerization, hybrid nanoparticles. Upon drying, these particles form films. In this study, we focused on the properties of such hybrid materials for pressure sensitive adhesives (PSA).

Acrylic PSA (Satas 1989; Jovanovic 2004) are generally weakly crosslinked copolymers of low T_g which have insoluble (gel) and soluble (sol) fractions. A very broad molar mass polydispersity of the sol fraction and a cohesive network formed by the gel is a good and relatively easy way to achieve a practical solution, but has limitations due to the impossibility to independently control the architecture of the sol and gel fractions during a simple synthesis. The fine control of the network structure of the gel becomes an essential aspect of advanced techniques to achieve a better balance of properties.

A possible design path to achieve a better control of the network structure is to incorporate another polymer (like alkyd or polyurethane) to form hybrid materials. The preparation of these hybrid materials could potentially bring a more favorable balance of properties compared to the initial purely acrylic PSA.

Materials

All samples were prepared by miniemulsion polymerization. The monomer composition of the acrylic matrix was: butyl acrylate (BA) 89.5 wt%, methylmethacrylate (MMA) 9.5 wt% and acrylic acid (AA) 1 wt%. A NCO terminated polyurethane (PU) prepolymer (Incorez 701, Industrial Copolymers Limited) was incorporated in the acrylic polymer particles. This incorporation was performed in three steps:

1) The PU prepolymer chains were dissolved in the organic monomer phase, which also contained the hydrophobe costabilizer octadecyl acrylate (ODA) and hydroxyl ethyl methacrylate (HEMA).

2) Bisphenol A (BPA) was added to the organic phase containing PU.

3) The organic phase containing the monomers and the HEMA-functionalized BPA-extended PU chains was added to the aqueous solution containing surfactant (Dowfax 2AI). Nanodroplets were formed by ultrasonication. The radical polymerization started with the addition of a redox initiator pair (Tertiary Butyl HydroPeroxide, TBHP, and Sodium Formaldehyde Sulfoxylate, SFS). Miniemulsion polymerization was carried out in batch.

1-dodecyl mercaptan was used as a chain transfer agent (CTA), and 0.2 % was added in all formulations. Octadecylacrylate (ODA) was used as hydrophobic component and was added to the particles to avoid Ostwald ripening (Landfester 2001). Two series of samples were prepared. In the first series, the molar ratio between OH and NCO functions was equal to 0.55, and the molar ratio of OH functions coming from HEMA over OH functions coming from BPA (the so-called HEMA/BPA ratio) was kept equal to 0.22. The polyurethane weight fraction was changed from 5 wt% to 50 wt%. In the second series, a fixed quantity of PU (25 wt%) was incorporated into the particles. The ratio OH/NCO was fixed at 0.55 and the ratio HEMA/BPA was changed from 0.11 to 0.50. Finally, one blank latex with no PU, no HEMA and no BPA was prepared with a CTA content of 0.2. Final latexes with ~ 100nm diameter particles were prepared. Adhesive films were obtained through the drying of such latexes[1]. After a drying step at room temperature and then at 110°C, adhesive soft films were obtained. We will present here the results obtained for a monomer composition of butylacrylate, methylmethacrylate and acrylic acid in such wt proportions: 89.5/9.5/1.

Experimental techniques

Probe-tack tests[2] were carried out on thin films (around 100µm thick) dried on glass slides. The analysis of $\sigma=f(\varepsilon)$ curves and movies obtained through this experiment provide the information to evaluate the adhesive properties of the sample[2],[3].

Adhesive properties can be completed with rheological measurements in the small strain range and tensile tests in the large strain regime. These experiments were performed in a standard parallel plate rheometer on thicker films (500µm in average) at 8% of strain.

Finally, the polymer network structure was characterized for gel content and swelling capability. These measurements were made gravimetrically. Dried films were swollen and dissolved in tetrahydrofuran (THF) during a week and weighed before and after dissolution.

Results

We present here the results of waterborne adhesive films made from acrylic-urethane hybrid particles. Two parameters were mainly varied: the amount of polyurethane compared to the monomer content, and the ratio between the grafting agent and the chain extender. In both series, the films were transparent without any cracks or bubbles indicating that homogeneous films at the macroscopic scale were obtained. As for mechanical properties, the two parameters have different effects. The tack results for different amount of PU with a ratio grafting/extension of 0.11 are shown on Figure 1.

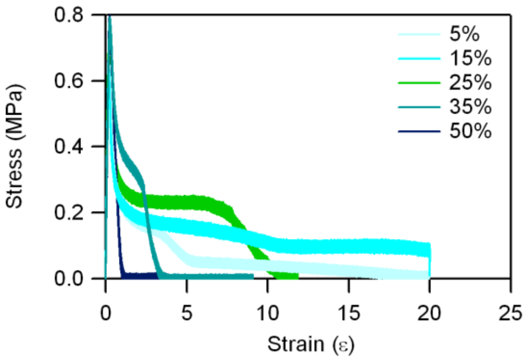

Figure 1: Tack curves for different amounts of PU and grafting/extension=0.11; v_{deb} = 100 µm/s.

We can see in the tack curves that an increase in the rate of polyurethane dramatically changes the adhesive strength. For very small amounts of PU (5% and 15%), the samples behave like a highly viscous liquid. There is a soft cohesive debonding. On the contrary, with 35% and 50% of polyurethane, the samples are very elastic and hardly deformable. As a result, there is no fibrillation but interfacial propagation of cracks at the probe/sample interface. The optimal adhesive properties are finally obtained for ~ 25% of PU.

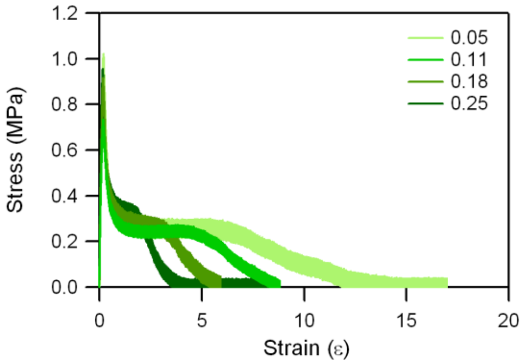

Figure 2: Tack curves for different ratios grafting/extension and PU=25%; V_{deb} = 100 µm/s.

If the amount of PU is kept fixed at 25% relative to the total monomer, but different ratios grafting/extension are used, the adhesive properties change differently. Increasing the rate of grafting does not drastically change the small strain modulus. Even for higher grafting ratio, fibrillation debonding is maintained, but the higher the ratio, the higher the plateau stress. This indicates that the large strain stiffness of the sample increases. Rheology results are also presented in Figure 3:

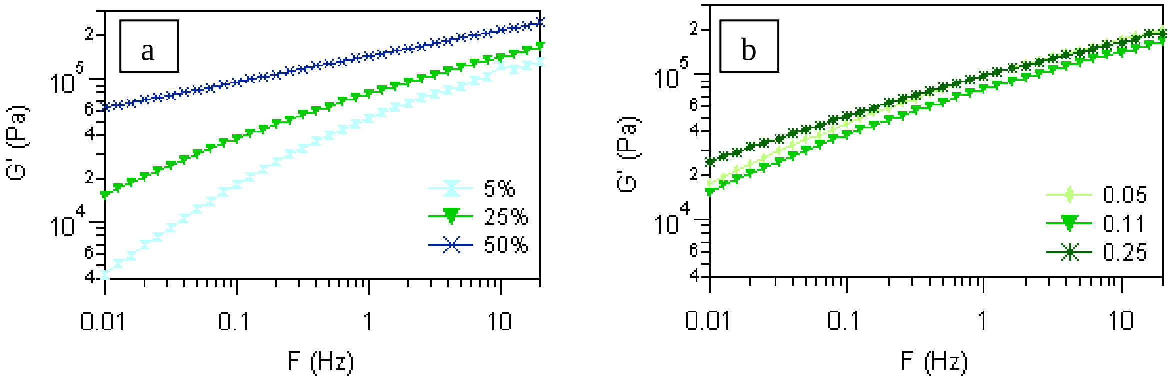

Figure 3: Rheology measurements: (a) for different amounts of PU and grafting/extension=0.11; (b) for different ratio grafting/extension and PU=25%; δ=8%

These curves are consistent with the tack results. At small strains, the most important effect is due to the amount of polyurethane.

If the two series of PSA are now subjected to large strains in tensile tests at a fixed crosshead velocity, the following results are obtained: As shown in Figure 4a, the increase in PU content at fixed grafting ratio leads to a significant change in both the density of entanglements (affecting the small strain elastic modulus) and the density of chemical crosslink points (affecting the large strain behavior). On the other hand, the increase in grafting ratio at fixed PU content only leads to a small increase in small strain modulus (the entanglement structure is nearly the same) but modifies the level of crosslinking and affects therefore the large strain behavior (Figure 4b).

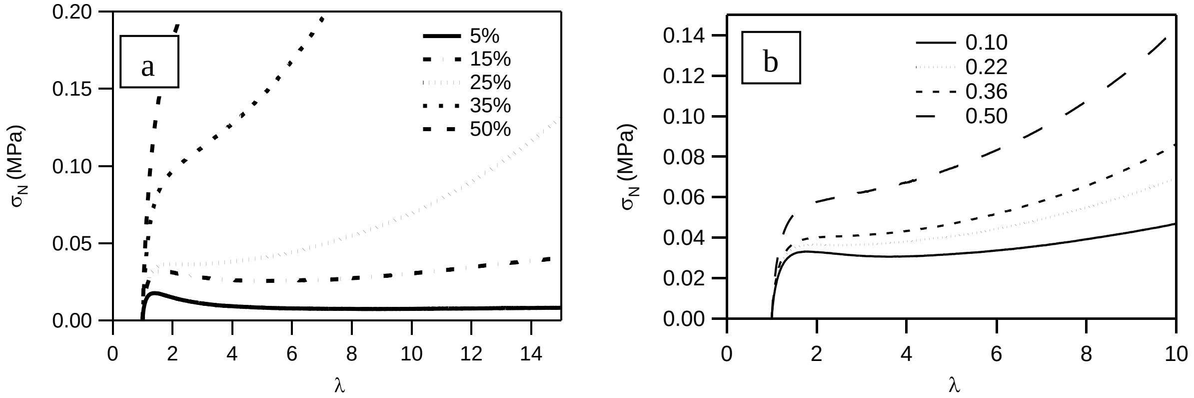

Figure 4: a) Nominal stress versus extension ratio λ at dε/dt=0.1s-1 for the 5 different PU weight fractions and b) Reduced stress versus 1/λ for the 4 different HEMA/BPA ratios; dε/dt=0.1s-1

Adhesive properties with standard tests

Results of the industrial standard tests (peel and shear resistance) are compared in Table 1. The adhesion energy corresponds to the area under the tack curve for test performed at a probe debonding velocity (V_{deb}) = 10 µm/s corresponding to an average initial strain rate dε/dt = 0.1 s^{-1}.

The addition of polyurethane strongly decreases the peel force. With a low fraction of PU, a transfer of adhesive from the PET substrate to the steel substrate indicates a poorly crosslinked sample, with high dissipation. With increasing PU content, the peel strength then decreases significantly. The quantitative differences between the probe tack results and the peel test results are due to the different strain rates (the peel tests are more equivalent to 1000 µm/s in tack experiments) and contact times. On the other hand, the shear resistance is improved by the addition of PU. Interestingly, there is a strong gap between shear resistance for 15 % and 25 % whereas adhesion does not decrease that much. Although there still is a cohesive failure for 25 %, we are in the range of interesting mechanical properties. However, the results indicate that it is not possible to have an increase of both peel and shear with this polymer architecture. Although PU offers a new way to organize the network, both properties are still strongly correlated.

Table 1: Adhesion energy measured for V_{deb} = 10µm/s and industrial shear and peel results

Sample	% PU	W_{adh} (J.m^{-2})^{a}	Shear resistance (min)	Peel (N/m)^{b}
0PU(0.2CTA)	0%	200.4 ± 21.2^{c}	181 ± 15 CF	436 ± 47
5PU(0.22)OH0.55	5%	67.5 ± 11.6	46 ± 15 CF	532 ± 47 CT
15PU(0.22)OH0.55	15%	164.3 ± 17.2	222 ± 15 CF	340 ± 47
25PU(0.22)OH0.55	25%	232.1 ± 65.9	9463 ± 15 CF	276 ± 47
50PU(0.22)OH0.55	50%	26.2 ± 11.5	> 10000	172 ± 47

a: for V_{deb}=10µm/s
b: at 300mm/min
c: for V_{deb}=100µm/s in that particular case

On the other hand, Table 2 compares the adhesion energy obtained with the probe-tack test at V_{deb} = 10µm/s to the industrial characterization for different HEMA/BPA ratios. These results are very interesting. Although the energy of adhesion measured by probe tack decreases slightly with the HEMA/BPA ratio, it never goes below that of the matrix with no PU. A certain level of adhesion is maintained regardless of the degree of grafting. In parallel, the industrial values of peel remain high in the range of ratios we have tested.

Finally—and this is the interesting conclusion—the shear resistance increases dramatically with the ratio HEMA/BPA.

Table 2: Adhesion energy measured at V_{deb} = 10 µm/s and industrial shear and peel results for the blank sample and the 4 HEMA/BPA ratios; in all cases OH/NCO=0.55

Sample	HEMA/BPA	Wadh ($J.m^{-2}$)	Shear resistance (min)	Peel (N/m)
0PU(0.2CTA)	0.0	200.4 ± 21.2	181 ± 15 CF	436 ± 47
25PU(0.11)OH0.55	0.11	265.4 ± 17.7	1680 ± 15 CF	284 ± 47
25PU(0.22)OH0.55	0.22	232.1 ± 65.9	9463 ± 15CF	276 ± 47
25PU(0.36)OH0.55	0.36	206.9 ± 49.4	> 10000	252 ± 47

Discussion

Based on these results, the amount of polyurethane clearly increases the elastic modulus at small strains. Since this increase is not due to a change in T_g, the polyurethane is significantly increasing the density of entanglements. To understand this result, one must keep in mind that all PSAs have a much larger density of entanglements than crosslinks[3]. This is necessary to produce the significant softening of the PSA in uniaxial extension which averages stresses in the vicinity of local stress concentrations. In turn, this stress redistribution prevents interfacial crack propagation and favors fibril formation[4-6].

On the other hand, the ratio grafting/extension controls the density of chemical crosslinks in the network. When the proportion of chain extender is lower, the length of the PU chains between two crosslinking points is shorter, and the permanent crosslink density increases while the density of entanglements remains the same.

As a result, when the grafting ratio increases, the small strain elastic modulus (controlled mainly by the entanglements) does not change very much, whereas the maximum fibrils extension decreases, indicating a lower average molecular weight between crosslinks. This decrease in maximum extensibility of the chains appears to influence strongly the shear resistance without significantly decreasing the peel force, making it a promising strategy to achieve a better balance of properties.

Conclusion

Waterborne homogeneous hybrid acrylic-urethane particles have been synthesized by miniemulsion polymerization and the transparent dry PSA films have been characterized. In these hybrids films, two important and, to a great extent independent, parameters affecting polymer architecture have been identified. The PU chains increase the elastic modulus by increasing the entanglement density, whereas the ratio between chain grafting and chain extension controls the density of crosslinks, changing above all intermediate and large strain properties. No direct evidence of phase separation can be identified and the samples are fully transparent. The increase in density of crosslinks due to the controlled incorporation of PU appears to be a promising strategy to increase the shear resistance of the PSA without losing much of peel force.

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