Mechanical Properties of adhesive films obtained from PU-acrylic hybrid particles

Journal:	Macromolecules
Manuscript ID:	ma-2011-000702
Manuscript Type:	Article
Date Submitted by the Author:	12-Jan-2011
Complete List of Authors:	Creton, Costantino; E.S.P.C.I., Laboratoire PPMD-UMR 7615 Degrandi-Contraires, Elise; E.S.P.C.I., Laboratoire PPMD Bourgeat-Lami, Elodie; Laboratoire de Chimie et Procédés de Polymérisation, LCPP - CNRS - CPE McKenna, Timothy; CNRS-LCPP (Laboratory of Chemistry and Processes of Polymerization) Udagama, Ravindra; CNRS-LCPP (Laboratory of Chemistry and Processes of Polymerization) Ouzineb, Keltoum; Cytec Surface Specialties

SCHOLARONE™
Manuscripts

**Part II: Mechanical Properties of adhesive films obtained from PU-acrylic
hybrid particles**

Elise Degrandi-Contraire,¹ Ravindra Udagama,² Elodie Bourgeat-Lami,² Timothy McKenna,² Keltoum Ouzineb,³ Costantino Creton^{1*}

¹Laboratoire de Physico-Chimie des Polymères et Milieux Dispersés, CNRS-UPMC-ESPCI Paristech, 10 rue Vauquelin, 75231 Paris cedex 05, France

²Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS UMR 5265, Laboratoire de Chimie, Catalyse, Polymères et Procédés (C2P2), LCPP group, 43 Bd du 11 Novembre 1918, F-69616, Villeurbanne, France.

³ Research and Technology, Cytec Surface Specialties, Anderlecht Street 33, 1620 Drogenbos, Belgium

Abstract

The mechanical and adhesive properties of films made from novel hybrid urethane/acrylic dispersions have been investigated. The adhesive films were obtained from the drying of bicomponent acrylic urethane latexes prepared by miniemulsion polymerization. Phase separation at the macroscopic scale was avoided by using a NCO end-functionalized polyurethane (PU) prepolymer and a hydroxy ethyl methacrylate (HEMA) reactive comonomer in the acrylic backbone¹. The effect of two compositional parameters on the mechanical and adhesive properties was specifically studied: the PU weight fraction and the degree of grafting of the PU prepolymer on the acrylic backbone, controlled by the ratio between grafting agent HEMA and chain extender Bisphenol A (BPA). Swelling, rheological, tensile and probe-tack tests were used in parallel with an analysis of the macroscopic adhesive properties of the films. Results show that the PU weight fraction modifies significantly the small-strain elastic modulus and the gel fraction in the latex particle while the ratio HEMA/BPA can be used to adjust the chain length of the PU incorporated in the network. This ratio affects significantly the finite extensibility of the PSA while causing only relatively small changes in the low strain elastic modulus and gel fraction. An increase in the degree of grafting at fixed PU content is found to improve the resistance to shear of the adhesive without reducing its adhesion energy in a peel or probe tack test.

Introduction

Pressure-sensitive adhesives (PSA) are soft polymeric materials displaying an instantaneous adhesion on most surfaces upon application of a light pressure. Although the function appears relatively simple, the design of proper PSA is complex and relies heavily either on polymer chemistry (for acrylic and silicone polymers) or on formulation (for block copolymers and natural rubbers) in order to obtain sparsely crosslinked polymer networks with optimized properties²⁻⁷. This optimization means that the PSA must be able to dissipate energy during the peeling process (a property optimized for a highly viscous entangled polymeric liquid) and must be resistant to creep in shear (optimum when some crosslinking is present preventing flow).

Acrylic PSA^{4, 8} are generally weakly crosslinked copolymers of low T_g which have insoluble and soluble fractions, respectively called gel and sol. A very broad molar mass distribution (i.e. high 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 of independently control the architecture of sol and gel 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 (such as an alkyd or a polyurethane) to form hybrid materials. The preparation of these hybrid materials could potentially lead to a more favourable combination of properties compared with those of the initial purely acrylic PSA. Because of environmental concerns however, we have focused our study on emulsion-based acrylic PSA⁸. In emulsion-based systems, the independent control of the network structure of the gel and of the sol fraction is more difficult. Furthermore, the control of the interfaces between particles remaining after drying is problematic and can strongly affect the mechanical properties^{9, 10}.

However, the development of miniemulsion polymerization^{11, 12} has helped to overcome the main issue of the homogeneous incorporation of a hydrophobic polymer in a waterborne acrylic polymer. The advantage of miniemulsion polymerization is that it is possible to directly incorporate a hydrophobic polymer (e.g. PU) into the monomer droplets during the droplet formation step, and then directly polymerize the droplets to get a hybrid where the components are mixed on the scale of nanometers¹². If these hydrophobic compounds contain

reactive functional groups, such as unsaturated double bonds, then they can be chemically incorporated into the growing polymer chains during the free radical polymerization.

Many different components have been incorporated successfully into hybrid systems in this manner, and several reviews are available presenting the technique and the possibilities of hybridization¹¹⁻¹⁴.

A number of studies have investigated the synthesis of acrylic-polyurethane (PU) systems. Successful incorporations have been reported by the formation of interpenetrating networks¹⁵, by the formation of a core-shell structure¹⁶ or by standard emulsion with a polyurethane dispersion as a seed¹⁷. In all cases, the transparency and homogeneity of the hybrid were better than those of the physical blends. However miniemulsion polymerization appears to be a versatile and powerful method to graft polyurethane to an acrylic polymer as exposed in the work of Udagama *et al.*¹, of Wang *et al.*¹⁸⁻²² or again of Li, El-Aasser and coworkers²³. In the latter study, it is shown that the grafting prevents phase separation at the particle scale between polyurethane and acrylic copolymer. Most studies focused on applications as coatings, where advantages of combining acrylic with urethane for PSA applications are potentially numerous: better film-formation, better mechanical stability or temperature resistance²³⁻²⁵ and where a precise control of the polymer architecture is not necessary since crosslinkers (dryers) are often added. To the best of our knowledge ours is the first study focusing on acrylic polymers for adhesive applications where the control of the polymer architecture is essential to obtain the desired properties and where a precise control of a low level of crosslinking²⁶ and of the entanglement structure is essential²⁷.

In this study and in its companion paper¹, we selected a model acrylic copolymer typical of those used for PSA, and investigated the incorporation of a minority fraction of a low molar mass reactive PU in the acrylic particle. Part I¹ focuses on the synthesis methods while part II, the current paper, focuses on the effect of changing synthesis parameters on the adhesive properties and relates such changes to the network structure, characterized by mechanical tests on dry films and by swelling experiments.

Experimental

Synthesis

All samples have been synthesized in batch via miniemulsion polymerization. The details of the polymerisation procedure are described in a companion paper¹ and we only briefly recall here the main synthesis parameters which are necessary to understand the results.

The monomer composition of the acrylic matrix was: butyl acrylate (BA, 89.5 wt%), methyl methacrylate (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 hydrophobic costabilizer: octadecyl acrylate (ODA). Hydroxy ethyl methacrylate (HEMA) was added and a known amount of NCO functions was reacted with a known amount of HEMA. We thus define the percentage of HEMA to NCO (% HEMA to NCO). This step was conducted for 12 hours at 25°C using dibutyltin dilaurate as catalyst and results in the grafting of NCO to the HEMA.

2) A known amount of Bisphenol A (BPA) was added to the organic phase containing PU and the dibutyltin dilaurate catalyst and reacted for 30 minutes at 25°C. The role of this BPA was to extend the PU chains and complete the reaction with the remaining NCO groups.

3) The organic phase containing the monomers and the HEMA-functionalized BPA-extended PU chains were added to the aqueous solution containing surfactant (Dowfax 2AI). Nanodroplets were formed by ultrasonication. The radical polymerization was initiated with the addition of a redox initiator pair (Tertiary Butyl HydroPeroxide, TBHP, and Sodium Formaldehyde Sulfoxylate, SFS) and miniemulsion polymerization was carried out at 50°C.

1-Dodecyl mercaptan was used as a chain transfer agent (CTA) to control the kinetic chain length and therefore gel formation. 0.2 wt% with respect to monomers was added unless mentioned otherwise. It is important to note that butyl acrylate is much more prone than methylmethacrylate to chain transfer during free radical polymerization and naturally leads to branched architectures of the polymer in the absence of CTA, ODA was used as hydrophobic component and was added to the particles to avoid Ostwald ripening. Three

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 from the HEMA to OH functions from the BPA (the HEMA/BPA ratio) was kept equal to 0.22. The polyurethane weight fraction was changed from 5 wt% to 50 wt% based on monomers. In the second series, a fixed quantity of PU (25 wt%) was incorporated in the particles. The ratio OH/NCO was fixed at 0.55 and the ratio HEMA/BPA was changed from 0.11 to 0.50. In the last series, ODA was excluded from the synthesis and the ratio OH/NCO was increased to 1. Two samples with 25 wt% of PU were prepared with different HEMA/BPA (respectively 0.10 and 0.25) and different CTA contents (respectively 0.3 and 0.2). Finally, one blank latex with no PU, no HEMA and no BPA was prepared with a CTA content of 0.2%. Table 1 summarizes the important formulation parameters for the different samples.

Table 1. Description of the different series of latexes

Lab code	CTA ^a	PU ^b	HEMA (mol% to NCO)	OH/NCO	HEMA/BPA ^b
T150	0.2	5	10	0.55	0.22
T151		15			
T152		35			
T153		50			
T147		25	5		0.11
T145			10		0.22
T148			15		0.36
T149			20		0.50
T160	0.3	25	10	1	0.10
T161	0.2		20		0.25
T170	0.2	0	/	/	/

^a Wt% relative to monomers. ^b Molar ratio of the OH groups from HEMA to the OH group from BPA.

Polymer characterization

The solid content of the latexes was measured gravimetrically and was ~ 50 wt% of polymer for all latexes.

We measured the gel content and the swelling ratio, Q , by static measurements. A small piece of solid film was cut and weighed (W_1) and was then immersed in THF for a week. After a week, the sample which was completely swollen by the solvent was taken out and weighed again (W_2). It was then dried at 60 °C for 30 minutes to extract all the solvent and the dried sample was weighed (W_3).

The gel content was given by: $\%gel = \frac{W_3}{W_1} \times 100$ (1)

And the swelling ratio by: $Q = \frac{W_2}{W_3}$ (2)

The glass transition temperature of the final polymer samples (T_g) was measured by Differential Scanning Calorimetry (DSC; TA Instrument DSC 2920). Two cycles were performed at cooling and heating rates of 10 °C.min⁻¹. The T_g was obtained from the second cycle.

Mechanical characterization

Samples for the rheological and tensile experiments were prepared as follows: a given volume of latex was deposited in silicone moulds and dried at room temperature for one week. The moulds were covered with a bell-jar to protect them from dust. The volume of latex was calculated to give the required final film thickness depending on the latex solid content. After a week, the moulds were held for 5 minutes at 110°C. The samples were then removed, placed between low-release silicone papers and cut to the desired dimensions with a die-cutter.

For the probe-tack experiments, the latexes were deposited on microscope glass-slides also protected from dust by a bell-jar, and dried 48 hours at room temperature. They were finally dried for 1 minute at 110°C and the resulting films, with an average thickness of 120µm, were kept in plastic boxes before use. All samples were used within a week of preparation.

The linear viscoelastic properties of the adhesives were characterized with a rheometer RDAII using parallel plate geometry. Frequency sweeps (0.3-120 rad.s⁻¹) with an applied strain

between 5% and 10% were made on 500 μm thick samples of 8 mm as diameter at room temperature.

To analyze the large-strain behaviour, we used a standard tensile INSTRON machine (model 5565) equipped with a videoextensometer (model SVE). The machine uses a 10 N load cell with a resolution of ± 1 mN. Rectangular strips of 5 mm wide (w_0) with an average thickness (e_0) of the order of 500 μm were cut within the self-standing films. Individual values were controlled for each sample. The initial velocity of the crosshead was chosen to obtain an initial strain rate of 1 s^{-1} which is roughly equivalent to the initial strain rate applied during the adhesion tests and all tests were performed at room temperature. The force-displacement curve obtained is then converted to nominal stress $\sigma_N = F/A_0$ vs. stretch $\lambda = l/l_0$

The adhesive properties were characterized with two types of tests: a laboratory probe test^{28, 29} and a series of standard industrial tests. In the probe tack test, a stainless steel probe comes in contact with the adhesive layer deposited on a glass slide. After a set contact time, the probe is withdrawn at a constant velocity. A mirror is installed upon the glass slide and allows the visualisation of the debonding mechanism and the measurement of the real contact area for each sample. We used standard parameters for the temperature (Room Temperature), approach velocity ($V_{\text{app}} = 30\text{ }\mu\text{m.s}^{-1}$), contact time ($t_c = 1\text{ s}$) and contact force ($F_c = -70\text{ N}$). The debonding rate was varied between 1 and 1000 $\mu\text{m/s}$ but we report here only data for the debonding velocity ($V_{\text{deb}} = 100\text{ }\mu\text{m.s}^{-1}$) for the purpose of comparing materials. The force was measured by a load cell (250N, resolution 0.5 N). The displacement of the probe was measured with an LVDT extensometer (range 5mm, resolution 0.5 μm). The force and displacement for each curve were normalized by the contact area of the probe (as visualized with the camera) and by the initial thickness of the film to obtain a stress vs. strain curve which will be used to compare adhesive films.

The characterization of the adhesive properties of the films with industrial standard tests (FINAT) was carried out as follows. The latexes were dried on a polyester (PE) backing film during 3 minutes at 110 $^{\circ}\text{C}$ to obtain dry adhesive film thicknesses of 23 μm which are standard in industry. These adhesive + PE layers were then bonded to a stainless steel (SS) substrate.

The shear resistance was defined by measuring the holding time (in minutes) before failure of a 1 inch² adhesive layer to which a mass of 1 kg was applied (FINAT test method 8). The

8

maximum time measured was 10000 min. After this limiting time, the test was stopped. If a cohesive failure occurred, CF was noted along with the value of the holding time at failure. It is worth noting that for a commercial PSA, cohesive failure is neither desirable in the case of the shear resistance test nor in the case of the probe test.

Results and discussion

Before discussing the specific effects of the PU weight fraction and of the degree of grafting, it is useful to briefly summarize the DSC results. The PU has no apparent effect on the heat capacity scans and a single T_g of -39 ± 3 °C is detected for all hybrid adhesive films. For comparison, the T_g of the pure PU is estimated to be around -48 °C. Therefore, the large distribution of the T_g of the copolymer and its proximity with the T_g of the PU could mask a possible phase separation.

1. Role of the PU weight fraction

1.1. Adhesive properties

In the first series of samples (sample T150 to T153 in table 1), the effect of the weight fraction of reactive PU incorporated in the polymer was investigated. Figure 1 presents probe-tack results for this series. The relevant parameters chosen to analyse these results were the plateau stress at intermediate and larger strain and the maximum strain. The plateau stress σ_f is related to fibrillation observed during the debonding, while the maximum strain $\epsilon_{\max}$ corresponds to the final detachment from the probe²⁸. Figure 1 shows that samples with a low amount of polyurethane (less than 25% based on the total amount of acrylic monomers) are characterized by a low fibrillation stress and a high maximum strain $\epsilon_{\max}$ ^a. The residues

^a For 15wt% of PU, the stress does not go back to zero for technical reasons. The maximum scale of the extensometer measuring the probe displacement is 5 mm. For the 15% sample, when the probe reaches 5 mm, fibrils joining the probe and the adhesive layer remain. These fibrils neither fail for a high deformation nor after waiting a long time. They can break cohesively or adhesively when the test is stopped and the probe is removed manually.

remaining on the probe after the test indicate a cohesive debonding inside the fibrils. These tack curves are characteristic of samples with a low level of elasticity, due to a low level of crosslinking. On the other hand, for samples with 35 wt% or 50 wt% of PU, the tack curves show almost no fibrillation plateau and the $\epsilon_{\max}$ is low. Despite nucleation of cavities at the onset of debonding, these cavities coalesce and interfacial propagation of cracks leads to an interfacial debonding^{30, 31}. Finally, the sample with 25% of PU forms a fibrillar structure upon debonding, and debonds at a maximum strain $\epsilon_{\max}$ of the order of 10 which is typical of many commercial PSA's. The final drop of the stress is characteristic of adhesive debonding, and results in the absence of residues on the probe. Thus, adhesive properties are best for this fraction of PU.

Figure 1. Stress-strain tack curves for the 5 PU weight fractions with 0.2% CTA and HEMA/BPA=0.22; $V_{\text{deb}}=100 \mu\text{m.s}^{-1}$ (i.e. $d\epsilon/dt=1 \text{ s}^{-1}$)

Table 2. Adhesion energy measured for $V_{\text{deb}}=100 \mu\text{m.s}^{-1}$ and industrial shear resistance results

Sample name	PU (wt%)	Gel fraction (%)	$W_{\text{adh}} (\text{J.m}^{-2})^a$	Shear resistance (min)
T170	0	47.3	200.4 ± 21.2	181 ± 15 CF
T150	5	Not measurable	161.4 ± 43.2 CF	46 ± 15 CF
T151	15	25.7	379.3 ± 111.3 CF	222 ± 15 CF
T145	25	37.4	284.9 ± 93.3	9463 ± 15 CF
T152	35	57.9	143.62 ± 39.9	Not measured
T153	50	73.8	49.6 ± 5.2	> 10000

^a For $V_{deb}=100 \mu m.s^{-1}$. ^b At $300 mm.min^{-1}$

Table 2 presents results from probe-tack tests, gel measurements and industrial shear tests. The comparison between probe test results, which measure the energy dissipated during fast debonding, and shear resistance, which is a measure of the resistance to failure at long times illustrates the difficulty in finding an optimum. Clearly the samples with 5 and 15% of PU are still dissipative but shear resistance is not much improved relative to the standard acrylic. The sample with 50% PU has an exceptional resistance to shear but does not dissipate much energy upon debonding. In the end the best compromise in properties appears to be the sample with 25% PU which combines an improvement in tack and a 50 fold increase in shear resistance. The most interesting result here is the comparison of the best hybrid PSA (T145) with the pure acrylic matrix (T170) showing that both adhesion energy and resistance to shear have been improved by the incorporation of the PU in the material.

The interpretation of these results requires a finer characterization of the differences in the network structure.

This characterization was carried out with the help of three different methods which are complementary: Rheological measurements reveal the level of viscoelasticity, large strain tensile experiments are a sensitive probe of the finite extensibility of the network chains and of the dissipation of energy taking place at large strains and the swelling and gel fraction measurements inform on the architecture of the polymer.

1.2. Linear viscoelasticity

Since decades the linear viscoelastic properties of pressure-sensitive-adhesives have been considered the best predictor of the adhesive properties³²⁻³⁵. From fully empirical criteria, we have now moved to more mechanistically based semi-empirical criteria which are able to predict to a certain extent the performance of PSA³⁰.

Figure 2 shows the variation of the storage modulus and $\tan\delta$ with frequency, for three adhesive films with increasing PU content. At equivalent degree of grafting, the more PU is added to the hybrid, the higher is its elastic modulus and the lower is $\tan\delta$. It is clear that the dissipation becomes much lower and frequency-independent in the presence of high PU contents. This shows that the number of pendant chains and free chains decreases

significantly with PU content. It also suggests that the entanglement density (at high frequency at room temperature) increases with PU content.

Figure 2. Evolution of G' (a) and $\tan\delta$ (b) as a function of frequency for different PU weight fractions: 5 wt% (T150), 25 wt% (T145) and 50 wt% (T153). $T = 25^\circ\text{C}$

These linear viscoelastic properties can be used to predict the suitability of the soft network for PSA applications. The value of the storage modulus at 1 Hz should be below 100 kPa to allow an easy contact with a rough surface³⁶. The value of $\tan\delta/G'$ at the relevant debonding frequency can be used as a finer criterion to predict whether fibrillation will occur or not upon debonding^{30, 37, 38}. For the sample with 50% of PU, the value of G' is $1.45 \cdot 10^5$ Pa, i.e. in the upper limit to conform to the surface. At the tack test frequency (1 Hz), the value of $\tan\delta/G'$ is $0.21 \cdot 10^{-5} \text{ Pa}^{-1}$, which is inferior to the lower limit of $0.5 \cdot 10^{-5} \text{ Pa}^{-1}$ reported to be required to have fibrillation debonding on steel^{30, 39}. The fact that $\tan\delta/G'$ is too low indicates a lack of dissipation coupled to a high value of the elastic modulus, completely consistent with the observed interfacial debonding.

Conversely, for 5% of PU, the storage modulus meets Dahlquist criterion ($0.53 \cdot 10^5$ Pa) and the level of dissipation is very high. As a result the debonding criteria is very high ($\tan\delta/G' \sim 1.15 \cdot 10^{-5} \text{ Pa}^{-1}$ at 1 Hz). Dissipation dominates and we are in presence of a highly deformable material which readily forms fibrils upon debonding. This is again consistent with the cohesive failure observed in adhesion tests.

As observed with the tack test, the value of 25 wt% of PU in the latex represents an optimum value for the viscoelastic properties as well. Indeed, both the stiffness and the fibrillation

($\tan\delta/G'$) criteria are fulfilled with $G'(1\text{Hz})$ equal to $0.99 \cdot 10^5 \text{ Pa}$ and $\tan\delta/G'$ equal to $0.6 \cdot 10^{-5} \text{ Pa}^{-1}$ at 1Hz, and fibrillation debonding is indeed observed.

The differences in viscoelastic behaviour reflect differences in the architecture of the polymer inside the particle. Table 2 gives the gel fraction in the adhesive film for the five PU contents. For 5% PU, the gel fraction is too low to be measured. Then it increases to 70-80% for the high PU-content samples.

The characterization of the gel fraction is a good indicator of the viscoelastic behaviour. The partially crosslinked gel imparts elasticity while the pendant chains attached to the gel and the sol fraction control the time dependent stress relaxation. Based on the differences in linear viscoelastic properties and gel fraction, the incorporation of PU at fixed grafting ratio increases the crosslink density, the entanglement density (high frequency G') and decreases the density of pendant chains and the soluble fraction..

1.3. Large strain behaviour

While linear rheology experiments are useful to predict whether fibrils will form or not after the initial cavitation stage, the final detachment of these fibrils can only be predicted through the analysis of the large strain behaviour⁴⁰⁻⁴². Figure 3 shows the results of tensile experiments for the five samples with different amounts of PU. Very significant differences due to the presence of PU are immediately apparent not only in the absolute values of the stress at equivalent strain but in the overall shape of the stress strain curve. The two samples with the lowest PU weight fractions (T150 and T151) do not present any hardening at large strain but simply flow at a nearly constant nominal stress.

Figure 3. Nominal stress versus lambda for the 5 different PU weight fractions; $d\varepsilon/dt=1s^{-1}$; the bottom figure is a magnification of the red square

As it is obvious from looking at the curves of Figure 3, the tensile behaviour of these weakly crosslinked networks is highly non linear, and shows a pronounced relaxation or softening after about $\lambda = 1.5$. For almost all PSA's this softening is both strain and strain rate dependent and curves measured at a single strain rate can be fitted equally well by a viscoelastic model²⁶ or by a nonlinear elastic model⁴³. However if tensile tests are carried out at two different strain rates with the same material, it is impossible to fit both curves with the same material parameters with either model. A quantitative modelling of the large strain behavior of a PSA would require a full fledged non-linear viscoelastic model including finite extensibility. Such

a model has not yet been developed. However it is possible to use a simpler and approximate methodology to characterize the PSA behaviour in large strain.

First the Young's modulus E_y can be measured at small strains. It is defined as the slope of a line fitting the curve between $\lambda=1$ and $\lambda=1.02$. This quantity represents the unrelaxed modulus and should be directly comparable with $G'(\omega)$ at the appropriate strain rate.

Second, the deviation of the stress-strain curve relative to the prediction from Gaussian rubber elasticity can be analyzed from the Mooney representation. The reduced stress σ_R , also named Mooney stress, is defined as:

$$\sigma_R = \frac{\sigma_N}{\left(\lambda - \frac{1}{\lambda^2}\right)}$$

It corresponds to the nominal stress normalized by $\left(\lambda - \frac{1}{\lambda^2}\right)$. For a Neo-Hookean rubber, the reduced stress is constant as a function of λ and is simply equal to the shear modulus G . For a PSA, this reduced stress is not constant and is typically represented as a function of the inverse of strain $1/\lambda$ ³⁰. Two characteristic parameters of the non-linear behaviour can be determined: the C_{soft} to characterize the softening at intermediate strain and the C_{hard} characterizing the onset of strain hardening at large strain³⁰. C_{soft} is defined as the slope of a line drawn between $(\sigma_R(0.8); 1/\lambda = 0.8)$ and $(\sigma_{R\text{min}}; 1/\lambda_{\text{min}})$. C_{hard} is defined as the reduced stress corresponding to the minimum in σ_R . Another interesting parameter is λ_{hard} , i.e. the strain level corresponding to the minimum reduced stress and hence to the onset of strain hardening. Strain hardening or more accurately strain stiffening⁴⁴ is correlated to the finite extensibility of the chains and thus to the network architecture. The ratio $C_{\text{soft}}/C_{\text{hard}}$ characterizes, in large strain the balance between relaxing and non-relaxing crosslink points and should be optimized for a PSA^{6, 30}.

The Mooney representations as a function of PU content are shown in Figure 4 while Table 3 gives the values of the viscoelastic parameters C_{soft} and C_{hard} , the ratio $C_{\text{soft}}/C_{\text{hard}}$ and the Young's modulus.

Fig.4: Reduced stress versus inversed lambda for the 5 different PU weight fractions; $d\varepsilon/dt=1\text{ s}^{-1}$; the bottom figure is a magnification of the region in the red square

Table 3. Values of the Mooney-Rivlin viscoelastic parameters for different PU amounts; $d\varepsilon/dt=1\text{ s}^{-1}$

Sample Code	PU (wt%)	C_{soft} (kPa)	C_{hard} (kPa)	$C_{\text{soft}}/C_{\text{hard}}$	E (kPa)
T150	5	84.5	No min in σ_R	∞	141.4
T151	15	115.9	No min in σ_R	∞	239.7
T145	25	109.4	11.8	9.3	275.6
T152	35	147.3	44.8	3.2	329.6

The ratio $C_{\text{soft}}/C_{\text{hard}}$ reflects the balance between the extent of relaxation at intermediate strain and hardening at large strain. It decreases significantly with increasing PU content, reflecting the less and less viscoelastic character of the films (see Figure 5). The Young's modulus is a small-strain high frequency modulus. It is affected by both chemical crosslinks and entanglements (that are all trapped at high frequencies). However in a fully acrylic matrix it is usually not much affected by a low level of crosslinking^{26, 43}. Its increase with PU content indicates that the network has clearly more entanglements with increasing PU. The increase of C_{hard} on the other hand only reflects the increase in chemical crosslinks. The non measurable density of such crosslinks for 5 wt% and 15 wt% of PU is fully consistent with the observed cohesive failure of these two adhesives in the tack experiments. The absence of strain stiffening at large strains prevents the fibrils from detaching from the surface without leaving residues. The T145 and T153 samples have values of C_{hard} and C_{soft} in the range of classic purely acrylic PSA's. The values of C_{hard} reflecting also the density of permanent crosslinks can be cross-checked also by a measurement of the swelling capacity of the gel fraction of the polymer.

Figure 5. Evolution of the gel fraction (■) and of the swelling ratio (△) with the polyurethane content

Figure 5 shows the change in gel fraction and equilibrium swelling of the gel as a function of PU content. The sharp increase in gel fraction with PU content is consistent with the viscoelastic measurements: the addition of PU reduces the uncrosslinked fraction and limits

relaxation from free chains and pendant chains. It also dramatically changes the equilibrium swelling of the gel which means that the density of elastically active chains (attached at both ends) in the gel increases significantly. Finally if the equilibrium swelling is compared in Figure 6 with the hardening strain λ_{hard} obtained from tensile experiments of the films. λ_{hard} decreases with the equilibrium swelling Q , which indicates that the PU chains considerably shorten the average length of the acrylic chains between crosslink points. This is due to the fact that, at fixed stoichiometry, more PU means more HEMA and hence more grafting points. Therefore the average molecular weight between grafting points on the acrylic chains decreases.

Figure 6. Evolution of the swelling Q with the hardening strain λ_{hard}

Summary

These combined results indicate that the network becomes much more densely crosslinked when the PU weight fraction increases. However it is interesting to note that a small amount of PU actually reduces the gel fraction and the strain stiffening, relative to a purely acrylic matrix. This reduction in crosslinking is probably due to a reduction in the acrylic kinetic chain length since the bisphenol-A favors chain transfer^{45, 46}.

The gel fraction and swelling experiments confirm that the NCO-terminated PU enhances crosslinking of the PU polymer chains to the acrylic network through the HEMA. In essence the PU would appear to act like any low molecular weight crosslinker.

Yet this is misleading because, in addition, PU chains are also more densely entangled than the acrylic chains because of the PPG constituting their soft segment ($M_e \sim 3 - 5 \text{ kg.mol}^{-1}$ for the PU⁴⁷ while $M_e \sim 20 - 30 \text{ kg.mol}^{-1}$ for the acrylics⁴⁸). Thus, the PU adds both chemical and physical crosslinks and this is the reason for the significant increase in the small-strain modulus. The very significant softening observed for all PU hybrids would be very difficult to obtain with a purely acrylic network.

The consequence on adhesive properties of this continuous variation in crosslinking and entanglement density with PU content is a clear transition from under-crosslinked to over-crosslinked materials. Only one of the adhesives gives a network architecture adapted to a PSA application and a reasonable balance between relaxation and hardening. This sample debonds adhesively in a fibrillation mode, with relatively high adhesion energy. An equivalent optimum in the PU weight fraction has been observed by Wang *et al.*²⁰ in the same type of PU/acrylic hybrid prepared for coating applications.

2. Impact of the degree of grafting of the PU

If the PU content is fixed, the second parameter that can be varied is the level of grafting of the PU chains to the acrylic matrix. The reaction between HEMA and NCO-terminated PU can be well controlled during the synthesis¹. In the following series, the fraction of NCO actually consumed during HEMA grafting is varied from 5 to 20mol%, taking into account that 20% is the maximum level of grafting allowed by the reaction between HEMA and PU¹. For a fixed total amount of OH groups, the degree of grafting is directly connected to the HEMA/BPA molar ratio. In this section, we compare samples with a constant weight fraction of PU (25%) and HEMA/BPA ratios changing from 0.1 to 0.5 with a ratio between OH and NCO fixed at 0.55.

2.1. Adhesive properties

Figure 7 shows the probe tack curves obtained for different degrees of grafting at a PU content of 25% and a CTA amount of 0.2%. For these synthesis conditions, a fibrillation plateau is always observed but cohesive failure of fibrils is sometimes observed for the sample with HEMA/BPA=0.10. The maximum deformation $\varepsilon_{\max}$ of the adhesive layer

decreases markedly when the ratio HEMA/BPA increases. A lower $\varepsilon_{\max}$ means that fibrils are less stretched at detachment and this is due to a combination of more strain stiffening and probably less dissipation near the interface⁴⁰. Conversely, the fibrillation stress σ_f of the tack curves increases with HEMA/BPA.

Figure 7. Stress-strain tack curves for 4 different HEMA/BPA ratios; $V_{\text{deb}}=100 \mu\text{m.s}^{-1}$ (i.e. $d\varepsilon/dt = 1 \text{ s}^{-1}$)

Table 4 compares quantitatively the adhesion energy obtained with the probe-tack test at $V_{\text{deb}} = 100 \mu\text{m.s}^{-1}$ to the results of the shear resistance tests for different HEMA/BPA ratios. The low grafting regime is particularly interesting. While increasing the adhesion energy relative to the pure acrylic matrix, the resistance to shear increases dramatically. Similar to the effect of PU content it is now interesting to examine the effect of the HEMA/BPA ratio on the network architecture.

Table 4. Adhesion energy measured at $V_{\text{deb}} = 100 \mu\text{m.s}^{-1}$ and industrial shear and peel results for the blank sample and the 4 HEMA/BPA ratios; in all cases $\text{OH/NCO}=0.55$.

Sample name	HEMA/BPA	W_{adh} (J.m^{-2})	Shear resistance (min)
T170	0.0	200.4 ± 21.2	$181 \pm 15 \text{ CF}$
T147	0.11	548.4 ± 128.2	$1680 \pm 15 \text{ CF}$

T145	0.22	284.9 ± 93.3	$9463 \pm 15CF$
T148	0.36	164.6 ± 21.3	> 10000

2.2. Linear viscoelastic properties

G' and $\tan\delta$ as a function of frequency for different HEMA/BPA ratios with 25 wt% of PU are shown in figure 8. Above 1 Hz, both change little with the ratio HEMA/BPA and are in the acceptable range for PSA applications. The resulting values of $\tan\delta/G'$ are all predicting a fibrillation debonding (from $0.44 \cdot 10^5 \text{ Pa} \cdot \text{s}^{-1}$ for the lower HEMA/BPA (T147) to $0.40 \cdot 10^5 \text{ Pa} \cdot \text{s}^{-1}$ for the higher ratio (T149)). In conclusion changes of the grafting ratio at fixed PU content do not greatly affect the linear viscoelastic properties.

Figure 8. Evolution of the G' (a) and of the ratio $\tan\delta/G'$ (b) as a function of frequency for HEMA/BPA=0.10 (T147), for HEMA/BPA=0.22 (T145) and for HEMA/BPA=0.50 (T149); $\varepsilon \sim 8 \%$.

This relative insensitivity of the linear viscoelastic properties with grafting ratio are confirmed by the gel fraction measurements which all show a gel fraction varying between 36 and 54 % and increasing slightly with increasing HEMA/BPA ratio.

2.3. Large strain experiments

The tensile experiments are more sensitive to the subtle changes in polymer architecture and they have been performed on the same samples at a nominal strain rate $d\varepsilon/dt=1\text{s}^{-1}$. To emphasize these fine changes, we choose here the Mooney representation, as explained in 1.3 (Figure 9). The different curves have a similar shape for all the HEMA/BPA ratios. The main

difference is in the onset of strain hardening, as can be seen on the magnified curve (fig. 9-right). From the Mooney plot, one can observe that C_{soft} and λ_{hard} do not change much but C_{hard} does. The increase of C_{hard} shows that HEMA/BPA mostly affects the density of permanent crosslinks, i.e. the bridges created by the PU chains, but not the finite extensibility of the network presumably controlled by the longer chains of the acrylic network. Such an apparently conflicting result can only be obtained with a heterogeneously crosslinked network, i.e. some densely crosslinked zones (which swell less and provide stiffness) and some less crosslinked zones which percolate and can extend. The values of C_{soft} (Table 5) remain relatively constant except for the lowest grafting density where the relaxation is very fast and as a consequence the value of $C_{\text{soft}}/C_{\text{hard}}$ decreases with grafting density. This decrease in viscoelastic character combined with the increased level of strain stiffening causes the differences in adhesion energy that are observed.

Measurements of the gel fraction (relatively constant for HEMA/BPA between 0.1 and 0.36) confirm this scenario: equilibrium swelling from $Q = 85$ at low grafting to $Q = 55$ at high grafting. Finally because the PU fraction is fixed the density of entanglements is also fixed and the small strain modulus slightly changes.

Figure 9. Reduced stress versus $1/\lambda$ for the 4 different HEMA/BPA ratios; $d\varepsilon/dt=1\text{ s}^{-1}$; the bottom figure is a magnification of the red square.

Table 5. Values of the Mooney-Rivlin viscoelastic parameters for the 4 different HEMA/BPA ratios; $d\varepsilon/dt=1\text{ s}^{-1}$

Sample name	HEMA/BPA	C_{soft} (kPa)	C_{hard} (kPa)	$C_{\text{soft}}/C_{\text{hard}}$	E_y (kPa)
T147	0.11	67.9	8.9	7.7	191.5
T145	0.22	109.4	11.8	9.3	275.6

T148	0.36	106.5	15.65	6.8	244.7
T149	0.50	116.2	26.9	4.3	414.9

Summary

The crosslinked network architecture is modified by the HEMA/BPA ratio but differently than by the PU content. Decreasing the HEMA/BPA ratio is equivalent to decreasing the density of PU bridges incorporated in the network. However this time this change occurs mostly in the gel fraction and does not greatly affect the finite extensibility of the network probably because of a heterogeneous gel structure. As a result, the adhesion energy remains relatively constant but the material can be made a little less crosslinked (favourable for adhesion on low energy surfaces) or more crosslinked (favourable for high shear resistance).

One can conclude that at fixed 25% PU content, the change in grafting ratio affects the crosslinking density of more crosslinked domains in a heterogeneous gel structure and does not affect much the sol fraction. It affects the low frequency dissipation in the polymer network, improving the resistance to flow, and not the small strain and high frequency elasticity. It is then possible to use separate synthetic tools to adjust the storage modulus (PU fraction) and the finite extensibility (PU grafting).

3. Effect of the OH/NCO ratio

As described in a companion paper, during the miniemulsion synthesis, it is necessary to add a hydrophobic monomer to avoid Ostwald ripening of particles¹². Here 5.15 % in weight (relative to the monomer content) of octadecylacrylate (ODA) was incorporated in the recipe. In presence of this hydrophobic component, it was not possible to incorporate the total amount of BPA required to give a stoichiometric ratio OH/NCO = 1. For amounts higher than 50% of the theoretical amount, flocculation of the particles was observed during the synthesis¹.

The consequence for the polymer architecture and mechanical properties is that the PU chains are expected to be less extended by BPA. Furthermore, as no isocyanate can be observed by

^{13}C NMR, it is reasonable to assume that reaction with water occurs. In other words, the reaction of polyurethane prepolymer chains is not completely controlled.

To promote a total reaction of the remaining isocyanate with BPA, some samples have been prepared without costabilizer ODA and with $\text{OH}/\text{NCO}=1$. No flocculation was observed and some solid films have been prepared from these new latexes to evaluate the impact of the OH/NCO ratio on the mechanical properties and the polymer architecture. In these samples, 25 wt% of PU is incorporated and two grafting ratios of the PU were chosen: 20% (high grafting) and 10% (low grafting). CTA content also varied from 0.2% for the high grafting to 0.3% for the low grafting (see Table 1). Probe-tack and tensile results of four samples are presented in figure 10.

Figure 10. Probe tack (left) and tensile results (right) of samples with $\text{OH}/\text{NCO}=0.55$ and $\text{OH}/\text{NCO}=1$ for high grafting of PU (top; samples T149 and T161) and low one (down; samples T147 and T160); for probe-tack tests $V_{\text{deb}}=100\mu\text{m.s}^{-1}$ (i.e. $d\varepsilon/dt=1\text{s}^{-1}$); for tensile tests $d\varepsilon/dt=1\text{s}^{-1}$

As seen in Figure 10, the effect of the change in process is different in the case of high grafting level and low grafting level. Nevertheless, in both cases, the increase in the amount

of BPA has a positive effect. For high grafting the deformability of the sample is significantly improved. When a high degree of grafting of PU is used, the material synthesized with more BPA has a higher maximum extension before debonding while maintaining the level of plateau stress. Based on the previous conclusions, it is consistent with constant grafting and constant PU fraction. The tensile curves show a less pronounced softening for the sample with high BPA amount and a more progressive hardening at very large strains. The polymer network is more deformable with equivalent small-strain stiffness. Our hypothesis is that the presence of BPA may act there as a chain transfer and reduce the kinetic chain length of the acrylic, effectively making the hybrid network a bit more viscoelastic and extensible. This confirms the hypothesis of longer acrylic chains formed with the presence of a higher amount of BPA and thus higher deformability. The gel and swelling measurements partially confirm this interpretation. The gel content decreases from 54.5 % for OH/NCO=0.55 (less BPA) to 44.3 % for OH/NCO=1 (more BPA). On the other hand, the swelling increases from 57.0 (less BPA) to 74.6 (more BPA). Considering the extraction technique used to measure the gel content, values may appear closed but their trend is consistent with the other observations. Indeed, they indicate that the network is less crosslinked, but with only a small effect of the decrease in the gel fraction on the elasticity.

For low grafting, probe-tack tests show a longer plateau, due to a stabilized fibrillation process. In tensile experiments the softening takes place at a higher stress and hardening is more pronounced. These observations reflect that the material is less deformable with more BPA. In this case, it may be argued that the extension of PU chains by BPA can help to connect dangling chains together to create PU bridges and increase the gel content and thus the stiffness. Unfortunately, the extraction and swelling measurements could not be done due to the low level of crosslinking in the samples.

If the effect of the extension on the mechanical properties (see Figure 11) is clear in both cases, it is not easy to locate the transition from the first mechanism (reduction of acrylic chain length) to the second one (formation of new PU bridges) and the effect of reaction with water is also unclear.

On the point of view of the application as PSA, the best results in tack, peel and shear are obtained for hybrid latexes with 25% of polyurethane compared to the acrylic monomers, with OH/NCO=1, HEMA/BPA ~ 0.25 and 0.2% CTA.

4. General discussion: Network structure of the urethane/acrylic hybrids

Several molecular analysis have demonstrated three ideas¹. First, all NCO groups have reacted with HEMA, BPA or water. Then, SEC analysis and inverse titration have shown that the molar mass of the PU prepolymer is $\sim 3000 \text{ g.mol}^{-1}$, and finally it is known that only a maximum of 20mol% of NCO groups can react with HEMA. Therefore, PU chains can be incorporated in three different ways:

- BPA-extended chains which have reacted on both side with HEMA form bonded PU chains. After acrylic polymerization, these chains will be part of the gel fraction.
- BPA-extended chains which have reacted on only one side with HEMA are dangling chains. They are terminated either by a BPA or by an amine (obtained after reaction with water). These chains are connected to the acrylic backbone at only one side.
- BPA-extended chains which did not react with any HEMA are called free chains. They are part of the soluble fraction inside the particles.

These three types of chains coexist in the particles and their proportions and lengths obviously change according to the fraction of PU, the ratio OH/NCO and the ratio HEMA/BPA.

To have an appropriate representation of the architecture of the hybrid network inside particles, one has to take in account two other important parameters. The molar mass of the acrylic copolymers ($300\text{--}4000 \text{ kg.mol}^{-1}$ depending on the samples) is much higher than that of the PU, even extended. Then, assuming that the soft chain is mostly polyether (polypropylene glycol PPG), the PU chains are much more entangled than the acrylic ones. M_e for this type of PU has been found to be around $3\text{--}5 \text{ kg.mol}^{-1}$ ⁴⁷ when it is $\sim 20\text{--}30 \text{ kg.mol}^{-1}$ for the main monomer, butyl acrylate^{48, 49}

Taking in account the different connections of the PU chains, a schematic representation of the network is presented in Figure 11 (except that no reaction of NCO with water is shown).

Figure 11: Theoretical urethane/acrylic hybrid network

The presence of PU affects not only the viscoelastic balance but also the finite extensibility of the adhesive layer by connecting the acrylic backbones. As discussed above, even significantly extended PU grafted chains remain shorter than the acrylic chains. Moreover, most of the chains are bonded chains connected to the acrylic at both ends. In this context the onset of strain stiffening is controlled by the length of the acrylic chains between two grafting points. The change in mechanical properties as a function of grafting density suggest that the PU may not be distributed homogeneously in each particle, with some PU rich zones connected together by PU poor zones.

Two important caveats need to be mentioned here. First no reaction with water is considered in this description. In reality, some of the NCO functions will react with water during the miniemulsification process and the early stages of the synthesis reaction^{1, 23, 50}. This fraction may modify the architecture of the polymer.

Second, in all the discussions above, we have ignored the particle morphology and assumed implicitly a homogeneous incorporation of the PU. This is consistent with the appearance of the films which are clear, transparent and crack-free at least at macroscopic level. This is also in good agreement with the unique T_g measured by DSC. Nevertheless, the arguments above plead for the existence of heterogeneous structures and a phase separation occurring at the particle scale for 25 wt% of PU and a degree of grafting of 10 % cannot be ruled out. The possible existence of these nanodomains which are more crosslinked but are embedded in a

less crosslinked matrix polymer, seem to have little effect on the dissipation of energy during debonding but to greatly strengthen the resistance to shear of the material. This would also be consistent with a recently published study on nanostructured adhesives⁵¹

Conclusion

The key findings of our study can be summarized as follows:

The amount of polyurethane (at fixed OH/NCO ratio) affected strongly the ratio between soluble and insoluble parts because of the addition of crosslinking points between the NCO-terminated PU chains and the acrylic chains. Moreover, since the polyurethane is more entangled than the acrylic, it also affected the small strain elastic modulus with the incorporation of many entanglements, which behave like permanent crosslinks at high frequency but can relax at low frequency or high temperature.

The degree of grafting at fixed PU content (controlled by the ratio between the grafting agent HEMA and the chain extender BPA) plays an important role in the architecture of the insoluble part. The analysis of the tensile tests strongly suggest a heterogeneous particle structure with a minority of more crosslinked PU rich domains and a majority of less crosslinked and percolating PU-poor domains.

As a result of this heterogeneous structure, industrial standard tests on the adhesive properties of the PSA have shown a clear improvement in shear resistance while the adhesion energy remained acceptable for standard applications. This clearly showed that the detailed structure of the gel part of the PSA is as important as the gel fraction itself, a point which has been often neglected so far.

Clearly, the fine control of the polymer structure inside a particle with a bicomponent system remains very challenging. Several reactions compete kinetically and the final result is likely to depend on the details of the procedure and on the details of the composition such as amount of chain transfer agent used, nature of the initiator, and of course temperature of the reaction. Furthermore the materials studied here have been produced with a batch process relatively far from the conditions used in industrial applications.

Nevertheless the general trends discovered should be broadly applicable to the design of hybrid networks containing both polycondensation reactions and free radical polymerization. All previous publications on urethane/acrylic networks focused on high T_g coatings which have much less propensity to chain transfer reactions and are more sensitive to the details of

the interfaces between particles^{19, 20, 23}. To our knowledge this is the first study on the design of such a network in soft adhesives.

Acknowledgments

The EU Framework 6 Integrated Project NAPOLEON NMP3-CT-2005-01184 is acknowledged for the financial support provided to this project.

References

1. Udagama, R.; Graillat, C.; Degrandi-Contraires, E.; Creton, C.; Bourgeat-Lami, E.; McKenna, T. *submitted*.
2. Tobing, S. D.; Klein, A. *Journal of Applied Polymer Science* **2001**, 79, 2558-2564.
3. Tobing, S. D.; Klein, A. *Journal of Applied Polymer Science* **2001**, 79, 2230-2244.
4. Satas, D., Acrylic Adhesives. In *Handbook of pressure-sensitive-adhesives*, 2nd ed.; Satas, D., Ed. Van Nostrand Reinhold: New York, 1989; Vol. 1, pp 396-456.
5. Sobieski, L. A.; Tangney, T. J., Silicone Pressure Sensitive Adhesives. In *Handbook of pressure sensitive adhesives*, 2nd ed.; Satas, D., Ed. Van Nostrand Reinhold: New York, 1989; Vol. 1, pp 508-526.
6. Lindner, A.; Lestriez, B.; Mariot, S.; Creton, C.; Maevis, T.; Luhmann, B.; Brummer, R. *Journal of Adhesion* **2006**, 82, (3), 267-310.
7. Creton, C.; Hu, G. J.; Deplace, F.; Morgret, L.; Shull, K. R. *Macromolecules* **2009**, 42, 7605-7615.
8. Jovanovic, R.; Dubé, M. A. *Journal of Macromolecular Science Part C: Polymer Reviews* **2004**, C44, (1), 1-51.
9. Joanicot, M.; Wong, K.; Cabane, B. *Macromolecules* **1996**, 29, 4976-4984.
10. Keddie, J. L. *Materials Science & Engineering R-Reports* **1997**, 21, (3), 101-170.
11. Landfester, K. *Macromolecular Rapid Communications* **2001**, 22, (12), 896-936.
12. Asua, J. M. *Progress in Polymer Science* **2002**, 27, (7), 1283-1346.
13. El-Aasser, M. S.; Sudol, E. D. In *Miniemulsions: Overview of research and applications*, Roy W Tess Award in Coatings Symposium, Boston, MA, Aug, 2002; Boston, MA, 2002; pp 21-31.
14. Schork, F. J.; Luo, Y. W.; Smulders, W.; Russum, J. P.; Butte, A.; Fontenot, K., Miniemulsion polymerization. In *Polymer Particles*, 2005; Vol. 175, pp 129-255.
15. Hegedus, C. R.; Kloiber, K. A. *Journal of Coatings Technology* **1996**, 68, (860), 39-&.
16. Hirose, M.; Kadowaki, F.; Zhou, J. H. *Prog. Org. Coat.* **1997**, 31, (1-2), 157-169.
17. Kukanja, D.; Golob, J.; Zupancic-Vlant, A.; Kranjc, M. *Journal of Applied Polymer Science* **2000**, 78, 67-80.
18. Wang, C.; Chu, F.; Graillat, C.; Guyot, A. *Polymer Reaction Engineering* **2003**, 11, (3), 541-562.
19. Wang, C.; Chu, F.; Graillat, C.; Guyot, A.; Gauthier, C. *Polymers For Advanced TEchnologies* **2005**, 16, 139-145.
20. Wang, C.; Chu, F.; Graillat, C.; Guyot, A.; Gauthier, C.; Chapel, J. P. *Polymer* **2005**, 46, 1113-1124.

21. Wang, C.; Chu, F.; Guyot, A. *Journal of Dispersion Science and Technology* **2006**, 27, (3), 325-330.
22. Wang, C. P.; Chu, F. X.; Jin, L. W.; Lin, M. T.; Xu, Y. Z.; Guyot, A. *Polymers For Advanced TEchnologies* **2009**, 20, (3), 319-326.
23. Li, M.; Daniel, E. S.; Dimonie; Sudol, E. D.; El-Aasser, M. S. *Macromolecules* **2005**, 38, 4183-4192.
24. Hirose, M.; Zhou, J. H.; Nagai, K. *Prog. Org. Coat.* **2000**, 38, (1), 27-34.
25. Sebenik, U.; Krajnc, M. *Journal of Polymer Science Part A: Polymer Chemistry* **2005**, 43, 4050-4069.
26. Deplace, F.; Rabjohns, M. A.; Yamaguchi, T.; Foster, A. B.; Carelli, C.; Lei, C. H.; Ouzineb, K.; Keddie, J. L.; Lovell, P. A.; Creton, C. *Soft Matter* **2009**, 5, 1440-1447.
27. Zosel, A. *Colloid and Polymer Science* **1985**, 263, 541-553.
28. Lakrout, H.; Sergot, P.; Creton, C. *Journal of Adhesion* **1999**, 69, (3/4), 307-359.
29. Zosel, A. *Journal of Adhesion* **1989**, 30, (1-4), 135-149.
30. Deplace, F.; Carelli, C.; Mariot, S.; Retsos, H.; Chateauminois, A.; Ouzineb, K.; Creton, C. *Journal of Adhesion* **2009**, 85, 18-54.
31. Yamaguchi, T.; Koike, K.; Doi, M. *Epl* **2007**, 77, (6).
32. Turreda, L. D.; Sonoda, H.; Hatano, Y.; Mizumachi, H. *Holzforschung* **1991**, 45, (6), 461-466.
33. Tse, M. F.; Jacob, L. *Journal of Adhesion* **1996**, 56, 79-95.
34. Chang, E. P. *Journal of Adhesion* **1991**, 34, 189-200.
35. Yang, H. W. H.; Chang, E. P. *Trends in Polymer Science* **1997**, 5, (11), 380-384.
36. Creton, C.; Leibler, L. *Journal of Polymer Science Part B: Polymer physics* **1996**, 34, 545-554.
37. Carelli, C.; Deplace, F.; Boissonnet, L.; Creton, C. *Journal of Adhesion* **2007**.
38. Nase, J.; Lindner, A.; Creton, C. *Physical Review Letters* **2008**, 101, 074503.
39. Deplace, F. Adhésifs Nanostructurés en Voie Emulsion. University Paris VI, Paris, 2008.
40. Glassmaker, N. J.; Hui, C. Y.; Yamaguchi, T.; Creton, C. *European Physical Journal E* **2008**, 25, (3), 253-266.
41. Good, R. J. *Journal of Adhesion* **1972**, 4, 133-154.
42. Verdier, C.; Piau, J. M. *Journal of Polymer Science Part B-Polymer Physics* **2003**, 41, (23), 3139-3149.
43. Roos, A.; Creton, C. *Macromolecules* **2005**, 38, (18), 7807-7818.
44. Erk, K. A.; Henderson, K. J.; Shull, K. R. *Biomacromolecules* 11, (5), 1358-1363.
45. Grassl, B.; Alb, A. M.; Reed, W. F. *Macromolecular Chemistry and Physics* **2001**, 202, (12), 2518-2524.
46. Lopez, A.; Degrandi, E.; Creton, C.; Asua, J. M., Simultaneous Free Radical and Addition Miniemulsion Polymerization: Effect of the Diol on the Microstructure of Polyurethane-Acrylic Pressure Sensitive Adhesives. submitted to *Polymer*, 2010.
47. Florez, S.; Munoz, M. E.; Santamaria, A. *Macromolecules Materials Engineering* **2006**, 291, 1194-1200.
48. Tong, J. D.; Jerome, R. *Polymer* **2000**, 41, (7), 2499-2510.
49. Moghbeli, M. R.; Zamir, S. M.; Molaei, B. *Journal of Applied Polymer Science* **2008**, 108, (1), 606-613.
50. Wang, C.; Chu, F.; Guyot, A.; C., G.; F., B. *Journal of Applied Polymer Science* **2006**, 101, 3927-3941.
51. Bellamine, A.; Degrandi, E.; Gerst, M.; Stark, R.; Beyers, C.; Creton, C. *Macromolecular Materials and Engineering* **2010**, 295.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

For Review - Confidential - ACS