

# DESIGNED POLYMER PARTICLE ARCHITECTURES FOR WATERBORNE ACRYLIC PRESSURE SENSITIVE ADHESIVES

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## Abstract

Polymer emulsions used in pressure sensitive adhesives (PSAs) often have relatively simple particle structures, with surfactants and ionized or polar side chains on the particle surface surrounding a hydrophobic core. During drying these particles coalesce to form the PSA film yet boundary layers of hydrophilic components remain. These boundary layers are thought to compromise the performance of waterborne PSAs relative to solvent-borne PSAs which have more uninterrupted film structures.

Two alternative particle architectures were investigated for enhanced PSA properties. In the first, a pre-strained interpenetrating network was designed into each particle through a multistage polymerization process. Based on prior work, such a network was expected to favor polymer chain scission upon mechanical deformation of the film, leading to higher stress at break and higher observed peel force. In the second, structure was added to the particle surface by blending a soft PSA made with little or no surface acid with water-dispersible poly(acrylic acid)-block-poly(butyl acrylate). The copolymer was expected to adsorb onto the particle surface with ionized acrylic acid side chains extending into the aqueous phase. Upon film formation this particle structure was hypothesized to form a strong honeycomb network with a soft core which would increase cohesion without a concomitant decrease in adhesion. For both particle architecture designs, structural data and PSA properties were investigated to identify opportunities to improve the adhesion/cohesion balance of waterborne PSAs.

## Introduction

Waterborne pressure sensitive adhesives (PSAs) are the largest class of PSAs by production volume, and most waterborne PSAs are comprised of polymer dispersions in water. Typically, the major component of a PSA dispersion is a hydrophobic copolymer of acrylic, styrenic, or other vinyl monomers made by emulsion polymerization. The emulsion polymerization process utilizes hydrophilic components such as water-soluble monomers, water-soluble initiators, surfactants, rheology modifiers, and salts which remain in the final PSA dispersion either associated with the polymer particles or free in the aqueous phase.<sup>1</sup> Water-soluble monomers such as acrylic acid (AA) or 2-hydroxyethyl acrylate may copolymerize with more hydrophobic monomers so that the resulting polymer is amphiphilic, displaying hydrophilic groups on the polymer particle surface, or they may form hydrophilic polymers which remain dissolved in the aqueous phase. Common initiators such as persulfate salts form sulfate polymer end-groups which also occupy the polymer–water interface. Surfactants, added to PSA dispersions not only to aid polymerization but also to improve dispersion stability and coatability, are present both at particle surfaces and in the aqueous phase. Salts, such as buffers or polymerization byproducts, and rheology modifiers, which are often hydrophilic polymers, are further components of the aqueous phase of a typical PSA dispersion. The aqueous phase surrounds all of the polymer particles, and the charged and hydrophilic components on the particles provide electrostatic and steric barriers to particle coalescence.

As this dispersion is applied and dried to create a PSA tape, label, or other article, the evaporation of water diminishes the aqueous phase and brings the particles closer together.<sup>2</sup> Eventually the particles deform to create a void-free film with interdiffusion of polymer chains across the particle interfaces. Nonetheless, aqueous phase components such as surfactants, water-soluble polymer, and salts remain in the interstices between particles,<sup>3</sup> while hydrophilic functional groups on the polymer surface can form membranes between polymer particles in the ultimate film.<sup>2</sup> These hydrophilic domains create weak boundary layers between polymer particles which are thought to decrease adhesion, cohesion, and water resistance.<sup>4,5</sup> Moreover, polymer particles of waterborne PSAs derived by random emulsion polymerization generally lack defined internal structures.

In contrast, studies of biological materials reveal diverse hierarchical structures that often impart superior mechanical performance.<sup>6</sup> Two of these structural motifs built up in growing biomaterials are sacrificial bonds and hidden lengths. Sacrificial bonds break early in the deformation process, enabling hidden lengths in the backbone polymer to unfold prior to the ultimate rupture of the backbone. Both of these processes dissipate tremendous energy, and such sacrificial bond/hidden lengths motifs are found in many biomaterials including collagen, titin, tendon, and silk.<sup>6</sup> Although the pioneering work on artificial sacrificial bond networks was performed using hydrogels,<sup>7</sup> more recently Ducrot *et al.* demonstrated a tough elastomeric network employing sacrificial bonds.<sup>8</sup> To create the sacrificial bonds, a first network comprising 6–10wt% of the final material was polymerized from ethyl acrylate crosslinked with butanediol diacrylate (1.45–2.81 mol%) in solvent. The dried first network was then swollen to equilibrium with methyl acrylate and butanediol diacrylate (0.01 mol%) which were copolymerized *in situ* with UV initiation to create a double network. Finally, the swelling and polymerization process was repeated to create a triple network in which the first network contains pre-stretched chains which can cleave at sacrificial bonds to dissipate energy as the material is deformed. This hierarchical structure incorporating sacrificial bonds dramatically increased the toughness of the triple network material to the range of that of natural rubber, which benefits from the mechanism of strain-induced crystallization.<sup>9</sup>

An alternative approach takes advantage of the residual hydrophilic domains in films derived from waterborne dispersions to build a hierarchical structure. In a series of publications,<sup>10, 11</sup> Chenal *et al.* demonstrated that reversible addition–fragmentation chain transfer (RAFT) polymerization can be used to generate hydrophilic/hydrophobic diblock copolymers which assemble into core/shell latex particles and dry into tough films. In one example, the diblock copolymer PAA-*b*-PBA with poly(acrylic acid) at 3 kDa and poly(butyl acrylate) at 100 kDa (PBA) spontaneously forms a core-shell latex during polymerization of the PBA block in water. Upon drying, the PAA blocks assemble into a glassy percolating network surrounding the soft PBA cores. Accordingly, the resulting material has energy dissipating mechanisms both from the fracture of the percolating network and the viscoelastic response of the soft cores.<sup>11</sup> Using a similar approach, Gurney *et al.* prepared PAA-*b*-PBA with both blocks at approximately 6 kDa and blended this amphiphilic diblock copolymer with a PBA latex prepared by conventional surfactant-free emulsion polymerization.<sup>12</sup> The diblock copolymer adsorbs onto the surface of the PBA latex and dries into a film containing a PAA percolated network. Films prepared with the diblock copolymer exhibited superior tack and creep resistance versus those without it, and their properties could be adjusted by changing the pH of the latex. Nonetheless, blending of the diblock copolymer with an optimized PSA latex did not improve its tack, suggesting that the benefits of the diblock copolymer are not applicable to all PSAs.

Inspired by these cases of hierarchical structures improving the properties of soft materials, we explored methods to apply these concepts to waterborne acrylic PSAs made by emulsion polymerization. In one example, we attempted to build a sacrificial bond network into a PSA through multistage emulsion polymerization. In another, we studied blends of amphiphilic block copolymers with PBA-based PSAs to form percolated network structures for enhanced adhesion and cohesion.

## Experimental

### Preparation of PSA Dispersions by Multistage Emulsion Polymerization

The pressure sensitive adhesive dispersions were prepared by a multistage emulsion polymerization process in a parallel automated reactor. The principal monomer composition was 97% BA, 2% styrene, and 1% AA. Varying low levels of allyl methacrylate (ALMA) or divinylbenzene (DVB) crosslinkers were incorporated in some stages. The first stage comprising 40% of the total monomer by weight was polymerized by gradual addition of monomer with a persulfate initiator. After the first stage was complete, the latex was cooled and 30% of the total monomer was added in one portion for the second stage of polymerization, which employed redox initiation. After the second stage was complete, the latex was cooled and 30% of the total monomer was added in one portion for the third stage of polymerization, which employed redox initiation.

### Laminate Preparation from PSA Dispersions Prepared by Multistage Emulsion Polymerization

All samples were direct coated on a 2 mil PET film and closed with silicone release liner. The wet drawdowns were dried in a convection oven at 80°C for 5 minutes. The samples were coated at a coat weight of 20 gsm. The samples were conditioned in a controlled temperature and humidity room (23 °C, 50 % humidity) overnight prior to applications testing.

### Synthesis of Poly(acrylic acid)-Block-Poly(butyl acrylate) Diblock Copolymer

A modification of the method of Gurney *et al.*<sup>12</sup> was used in which the synthesis was run over two days with air quenching at the end of the PAA polymerization on the first day and re-initiation by 4,4'-

azobis(4-cyanovaleric acid) (ACVA) for polymerization of PBA on the second day. The product was analyzed by standard GPC, DSC, and NMR methods.

### Preparation of Pressure Sensitive Adhesive Dispersions with 0% and 1% AA

The pressure sensitive adhesive dispersions were prepared by a typical semi-continuous emulsion polymerization process using persulfate initiator and monomer compositions by weight of either 100% BA or 99% BA/1% AA.

### PSA Dispersion–Diblock Copolymer Blend Preparation

The PAA-*b*-PBA diblock copolymer (BCP) was dissolved in water to make an 11.7 wt% solids solution. Ammonia hydroxide solution (30%) was added to dissolve the polymer with final pH 9. The translucent solution was added at 1, 2, and 5 wt% solids basis to 50 g of each PSA latex and the pH of the final dispersion was adjusted with ammonium hydroxide.

**Table 1. Formulation of PSAs with Diblock Copolymer Solution (by weight)**

Formulation	0% AA PSA	Diblock Solution	1% AA PSA
0% AA PSA	50		
0% AA PSA + 1% BCP	50	4.27	
0% AA PSA + 2% BCP	50	8.55	
0% AA PSA + 5% BCP	50	21.37	
1% AA PSA			50
1% AA PSA + 1% BCP		4.27	50
1% AA PSA + 2 % BCP		8.55	50
1% AA PSA + 5 % BCP		21.23	50

### Laminate Preparation from PSA Dispersion–Diblock Copolymer Blends

All samples were direct coated on a 2 mil PET film and closed with silicone release liner. The wet drawdowns were dried at room temperature or in a convection oven at 80°C for 5 minutes or 50°C for 20 minutes. The samples were coated at a coat weight of 20 gsm. The samples were conditioned in a controlled temperature and humidity room (23 °C, 50 % humidity) overnight prior to applications testing.

### Atomic Force Microscopy (AFM) Imaging of PSA Films Including Diblock Copolymer Blends

All samples were direct coated and dried at ambient temperature to generate films. The film surfaces were imaged by AFM using the PeakForce QMN mode to generate material property maps.

### Peel Adhesion (PSTC Test Method 101)

Peel adhesion is the measure of the adhesive strength of the adhesive to the substrate. The peel adhesion is tested by applying a 1” wide strip to a chosen substrate (typically stainless steel (SS) or high density polyethylene (HDPE) panels) using a roller (4.5 lb roller, moving at 24 in/min). The adhesive is allowed to dwell on the panel for a set time (typically 20 min or 24 hr) and then peeled from the panel at 90° or 180° angle at 12 in/min using a universal testing system. The average force is reported along with the failure mode.

### Loop Tack (PSTC Test Method 16)

The Loop Tack test measures the initial or instant adhesion when the adhesive comes in contact with the substrate. A 1” strip is cut and folded over to form a loop, exposing the adhesive side. It is then placed in

between the jaws of the Instron and lowered at a rate of 12 in/min to the substrate such that a 1" x 1" area of the adhesive comes in contact with the substrate for 1 second. Then the adhesive is pulled away and the peak force to pull the adhesive away from the substrate is recorded along with the failure mode.

### **Shear (PSTC Test Method 107)**

Shear is a measure of the cohesive strength of the adhesive. A 1" x 1" sample is applied to a stainless steel panel and laminated using a roller (4.5 lb roller, moving at 24 in/min). The panels are mounted vertically on the shear tester at an angle of 2°. A 1 kg weight is hung to the bottom of the sample. The time to failure is recorded as the shear (in hours) along with the failure modes. Typically, the failure mode is cohesive, thus directly correlated with the internal strength of the adhesive.

### **Failure Modes**

Failure modes are abbreviated as follows:

- A: Adhesive
- C: Cohesive
- AFB: Adhesive failure from backing

## **Results and Discussion**

### **Synthesis of Multistage PSAs Designed for Hierarchical Network Architectures**

Construction of a sacrificial bond network in an emulsion polymer PSA required a different approach from that of Ducrot *et al.* which employed solvent and bulk polymerization.<sup>8</sup> Because emulsion polymerization takes place in discrete particles surrounded by an aqueous phase, we devised a strategy to form a strained sacrificial bond network within each particle. The first polymer network was created by gradual addition of monomer with thermal initiation consisting of 40% of the total monomer mixture of 97% BA/2% styrene/1% AA. Polymerization of this stage was stopped by cooling to inhibit the thermal initiator, and the second stage consisting of 30% of the total monomer was added all at once to swell the first stage and pre-stretch its polymer chains. The second stage was then polymerized with redox initiation. After completion of the second stage, another bolus of monomer amounting to 30% of the total monomer was added to further swell the first two stages. This third stage was also polymerized by redox initiation. As shown in Table 2, different levels of the crosslinkers ALMA and DVB were added to each stage as well in analogy to the butanediol diacrylate used by Ducrot *et al.* The multistage entry with 0.2 wt% DVB in the first stage and no added crosslinker in the second and third stages is the closest analogy to the crosslinking motif utilized by Ducrot *et al.* A control PSA with gradual addition of all of the monomer with thermal initiation in a single stage was prepared as well. In all cases, the polymerizations proceeded smoothly with good particle size control and low coagulum.

**Table 2. Composition and PSA Properties of Multistage PSAs**

Staging (wt% crosslinker per stage)	180° HDPE Peel (N/in)	180° SS Peel (N/in)	HDPE Loop Tack (N/in)	SS Loop Tack (N/in)	SS Shear (h)
Single (0)	1.3 (0.3) A	11.3 (0.9) A	4.6 (0.2) A	7.8 (2) A	166 (27) C
Multi (0/0/0)	0.8 (0.2) A	4.6 (0.2) A	3.2 (0.6) A	6.4 (2) A	48 (11) C
Multi (0/0.05/0.05) ALMA	0.5 (0.1) A	2.5 (0.3) A	2.8 (0.4) A	5.0 (1) A	165 (42) C
Multi (0.2/0.2/0.2) ALMA	0.4 (0.1) A	1.4 (0.3) A	2.5 (0.2) A	3.2 (0.6) A	>280
Multi(0.2/0.25/0.25) ALMA	0.4 (0.1) A	1.4 (0.3) A	2.5 (0.2) A	3.2 (0.6) A	>280
Multi (0.2/0.2/0) DVB	0.4 (0.1) A	1.8 (0.2) A	-	4.4 (0.4) A	80 (9) C
Multi (0.2/0/0) DVB	0.7 (0.1) A	4.4 (0.2) A	4.1 (2) A	7.2 (0.1) A	15 (2) C
Multi (0/0.2/0.2) DVB	0.7 (0.1) A	4.9 (0.2) A	4.7 (1) A	7.1 (0.3) A	19 (1) C
Multi (0.2/0.2/0.2) DVB	1.0 (0.4) A	4.0 (0.3) A	4.0 (1) A	5.6 (0.9) A	25 (4) C

All peel tests performed after 20 minute dwell. Standard deviation shown in parentheses.

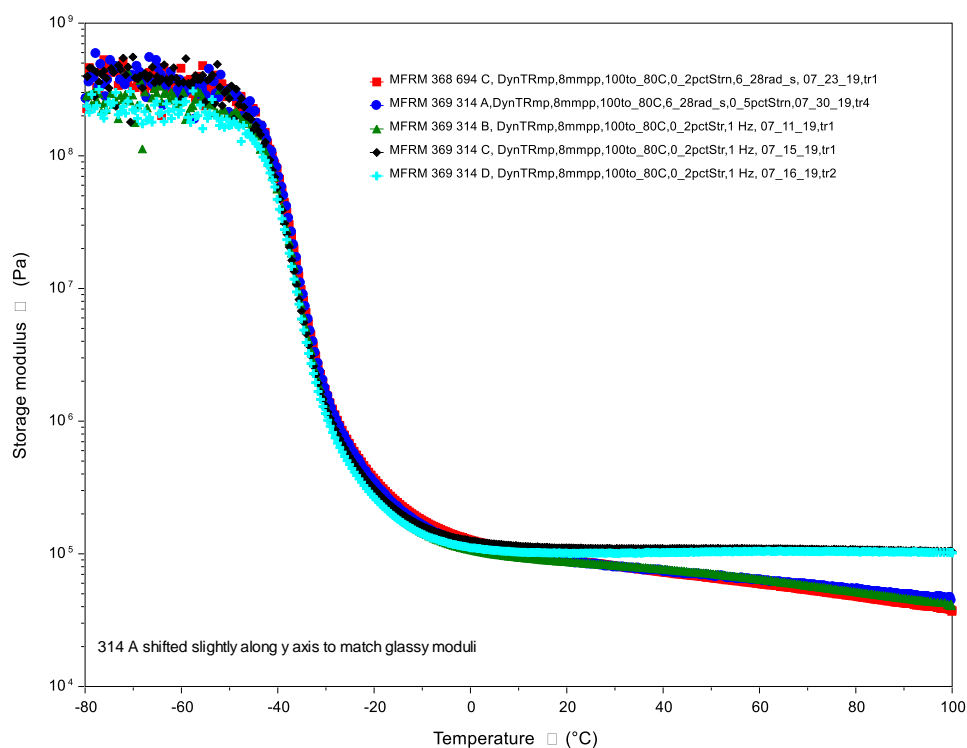
### Multistage PSAs Fail to Show Enhanced Adhesive and Cohesive Properties

Next, the multistage PSAs designed to contain sacrificial bond networks were tested for PSA properties to explore whether their architectures imparted enhanced adhesion or cohesion (Table 2). However, the control PSA made by a single stage process actually held the best balance of properties, with all adhesion measurements above or equal to all other samples and shear results among the best. The multistage control PSA made with no crosslinker had lower adhesion and shear than the single stage PSA, suggesting that the multistage thermal/redox process itself may negatively affect PSA properties. In comparison to the multistage control, all multistage samples employing ALMA had much higher shear and lower adhesion, likely indicating that the degree of crosslinking in these samples from even 0.05 wt% ALMA is too high for useful adhesion. Because the allyl group of ALMA is much less reactive than the methacrylate group, it typically does not react to form crosslinks until the concentration of vinylic and acrylic double bonds is very low.<sup>13</sup> Accordingly, in this multistage polymer, the ALMA may not have served to crosslink any of the stages independently to create sacrificial bonds and instead may have merely crosslinked the whole polymer particle at the end of the final stage. On the other hand, DVB, with two equivalent vinylic groups and similar structure to styrene, is expected to react efficiently during each polymerization stage. However, the samples prepared with DVB crosslinker generally did not have significantly different adhesion from the multistage control and had comparable cohesion. This suggests that the level of DVB was not high enough to generate a crosslinked network.

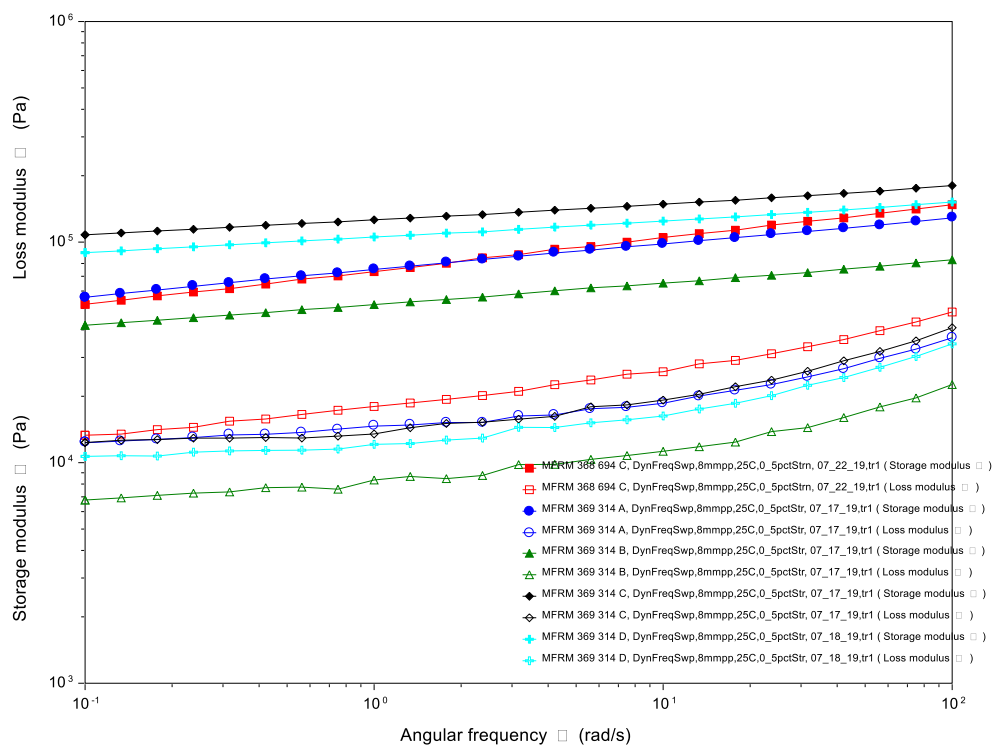
### Mechanical/Rheological Testing of Multistage PSAs Suggests No Sacrificial Network Structure

In order to understand the structure and properties of the multistage PSAs further, mechanical and rheological testing was performed on films generated from the PSA dispersions. Measurement of dynamic storage modulus ( $G'$ ) versus temperature for the control polymers and polymers with ALMA clearly shows crosslinking in the samples with 0.2 wt% or higher ALMA (Figure 1) in the flat response of  $G'$  at high temperature. The samples with no added crosslinker as well as the sample with 0.05 wt% ALMA have a downward slope in  $G'$  at high temperature which is consistent with less crosslinking. Figure 2 shows the plot of  $G'$  and  $G''$  (loss modulus) versus frequency for these samples as well. Interestingly, although the PSA properties of the single stage and multistage controls were very different, little difference is observed between these samples. The same measurements on samples containing DVB (Figure 3, Figure 4, and Figure 5) indicate that the differences between these samples and the multistage control are very subtle, with little or no crosslinking from DVB. These data do not indicate whether a sacrificial bond network is present in either the ALMA or DVB samples.

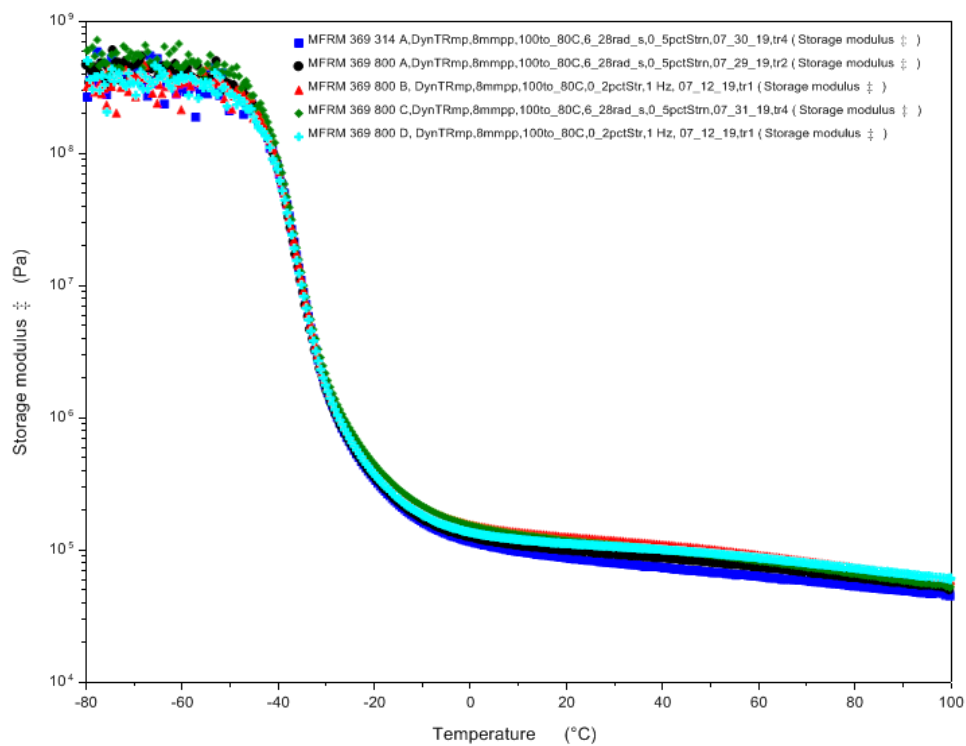
To provide further evidence for or against a sacrificial bond network, selected samples were subjected to a stress-strain in tension experiment in which the strain is increased linearly to a desired maximum value and then decreased linearly at the same rate. A similar experiment was performed by Ducrot *et al.* to demonstrate the signature behavior of sacrificial bonds in their triple network material.<sup>8</sup> The triple network had substantial hysteresis after the first cycle to a given strain which indicates dissipation by damage to the sacrificial bond network at high deformation. In contrast, the dual network material generated by Ducrot *et al.* followed the same path on each straining cycle with no hysteresis because the primary network chains were not fully pre-stretched to behave as sacrificial bonds.<sup>9</sup> For the multistage polymers generated by emulsion polymerization, samples with no crosslinker (Figure 6), ALMA crosslinker (Figure 7), and DVB crosslinker (Figure 8) demonstrated elastic responses following the same path on each strain cycle until sample failure. The performance of the no crosslinker and DVB crosslinker samples was very similar, indicating that the presence of DVB crosslinker had no appreciable impact on the stress-strain behavior of the PSA. On the other hand, the ALMA-crosslinked sample exhibited higher modulus and failed at lower stress than the uncrosslinked sample, as expected for a crosslinked material. None of the samples exhibit the hysteresis expected for a material with a sacrificial bond network.



**Figure 1.** Overlay of  $G'$  versus temperature for single stage control (red, 694C) compared with multistage control (blue, 314A) with no crosslinker, multistage with 0.05 wt% ALMA (green, 314B), and multistage with 0.2–0.25 wt% ALMA (black and turquoise, 314C and 314D).

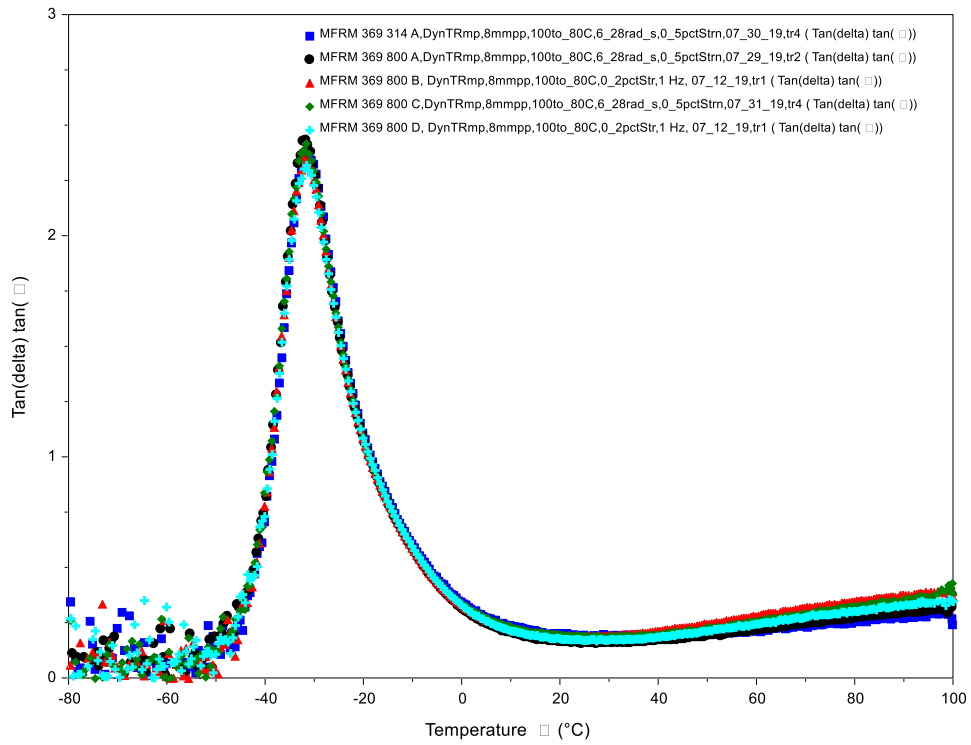


**Figure 2.** Overlay of  $G'$  and  $G''$  versus frequency for single stage control (red, 694C) compared with multistage control (blue, 314A) with no crosslinker, multistage with 0.05 wt% ALMA (green, 314B), and multistage with 0.2–0.25 wt% ALMA (black and turquoise, 314C and 314D).

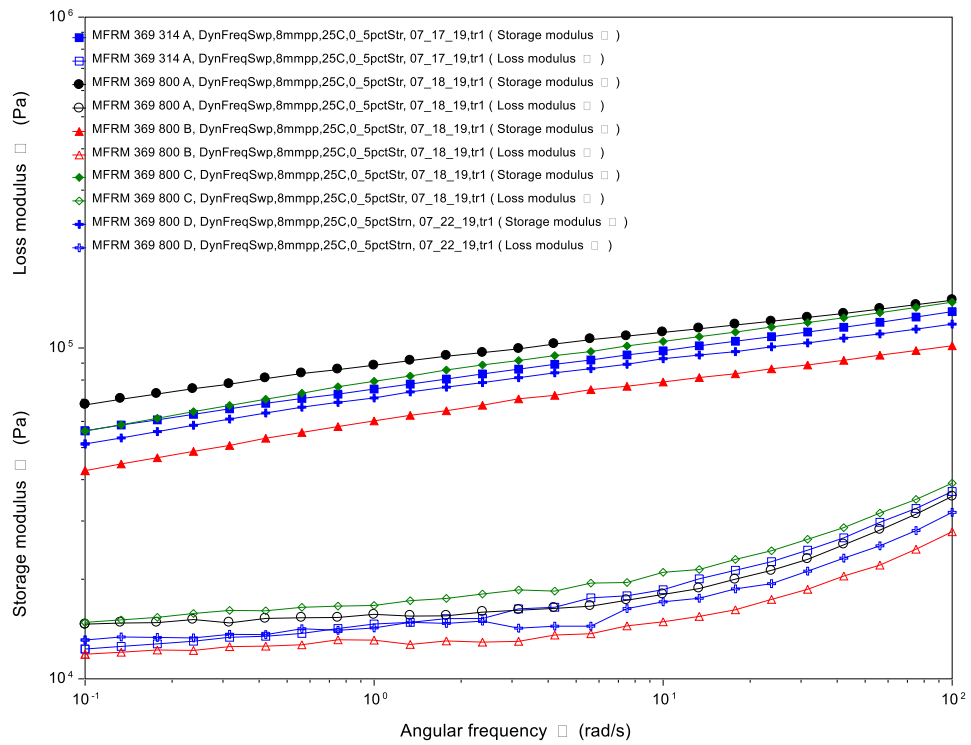


**Figure 3.** Overlay of  $G'$  versus temperature for multistage control (blue, 314A) with no crosslinker and multistage PSAs with DVB: 0.2/0.2/0, black, 800A; 0.2/0/0, red, 800B; 0/0.2/0.2, green, 800C; 0.2/0.2/0.2, turquoise, 800D.

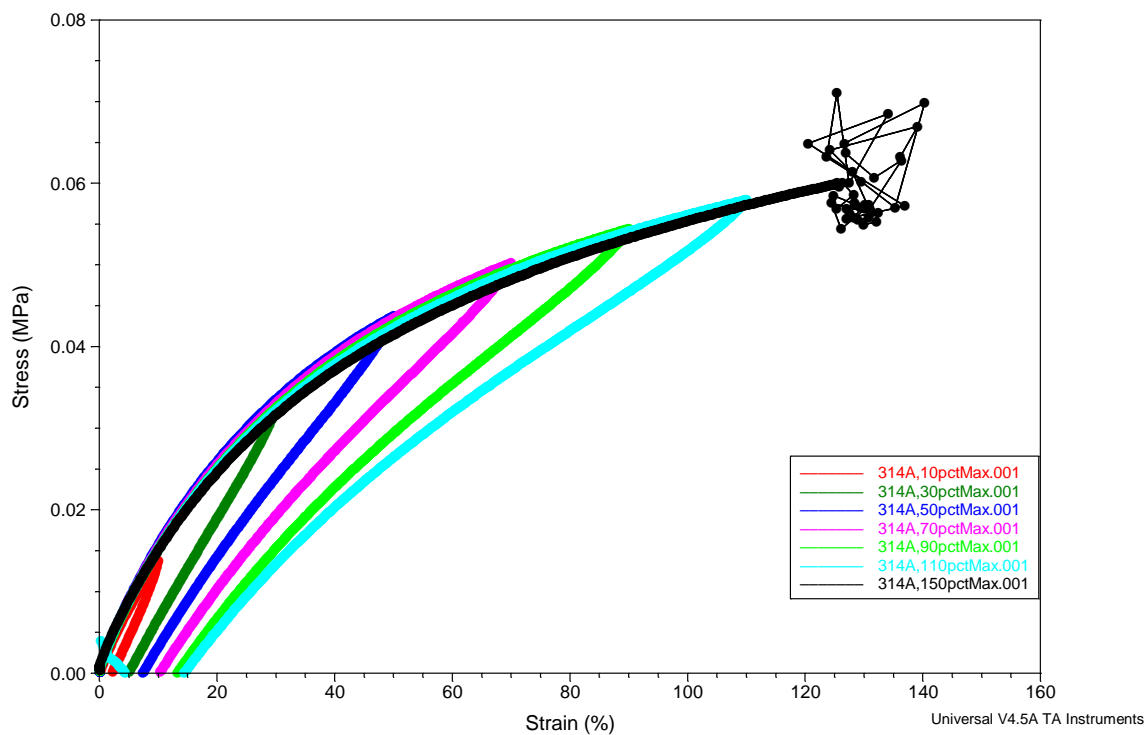




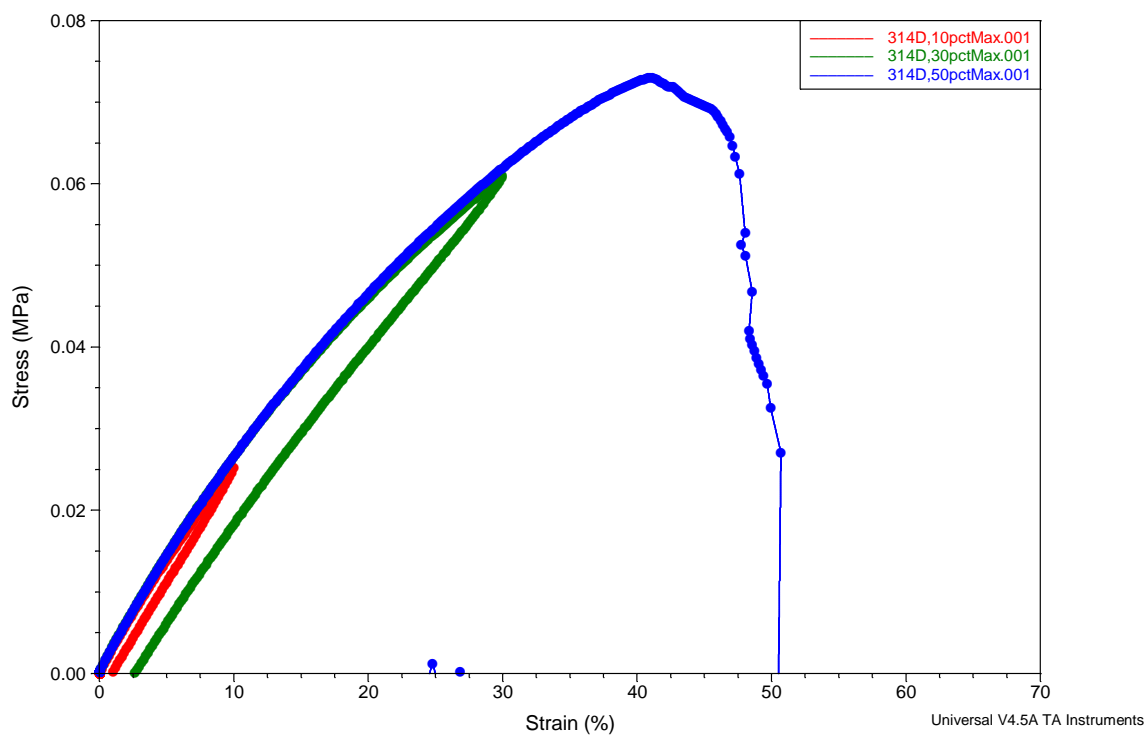
**Figure 4.** Overlay of  $\tan \delta$  versus temperature for multistage control (blue, 314A) with no crosslinker and multistage PSAs with DVB: 0.2/0.2/0, black, 800A; 0.2/0/0, red, 800B; 0/0.2/0.2, green, 800C; 0.2/0.2/0.2, turquoise, 800D.



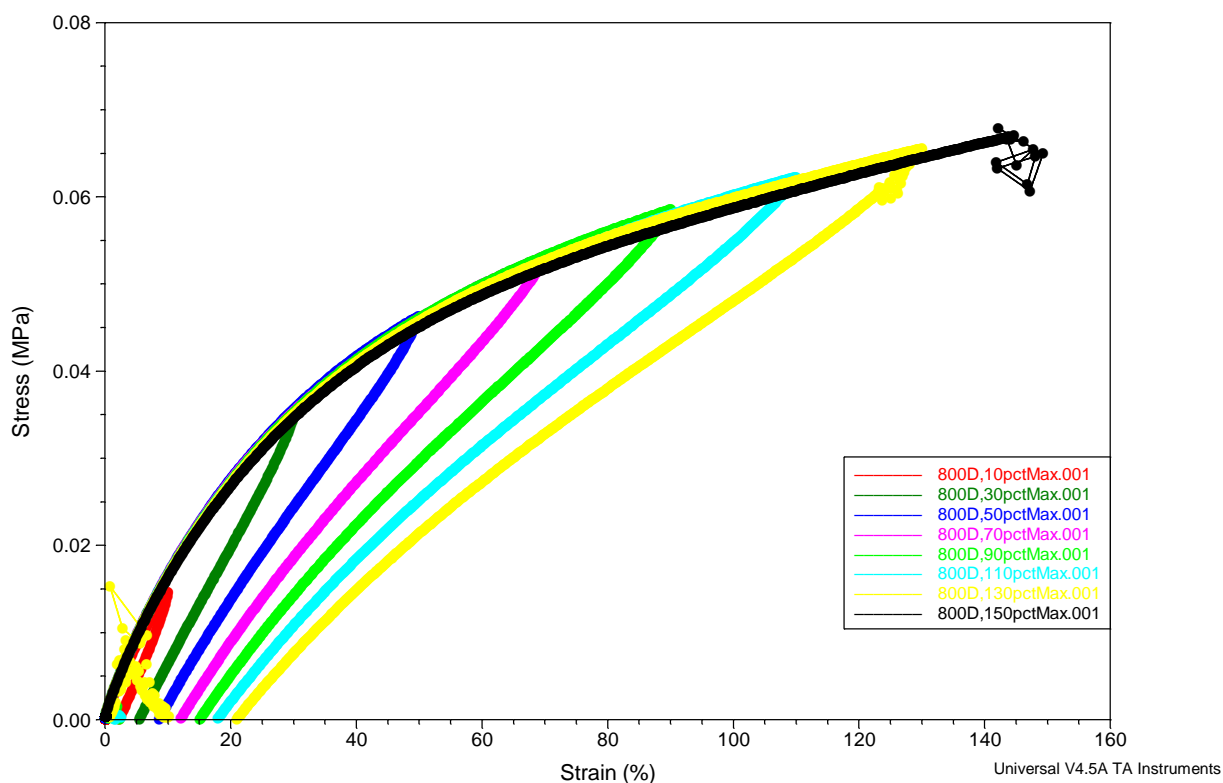
**Figure 5.** Overlay of  $G'$  and  $G''$  versus frequency for multistage control (blue, 314A) with no crosslinker and multistage PSAs with DVB: 0.2/0.2/0, black, 800A; 0.2/0/0, red, 800B; 0/0.2/0.2, green, 800C; 0.2/0.2/0.2, turquoise, 800D.



**Figure 6.** Stress versus strain cycles for multistage control with no crosslinker (314A) for set of strains from 10-150%, run in order of increasing strain on one sample which failed at 150% strain (black).



**Figure 7.** Stress versus strain cycles for a multistage PSA with 0.2/0.25/0.25 ALMA (314D) for set of strains from 10 to 50%, run in order of increasing strain on one sample which failed at 50% strain (blue).

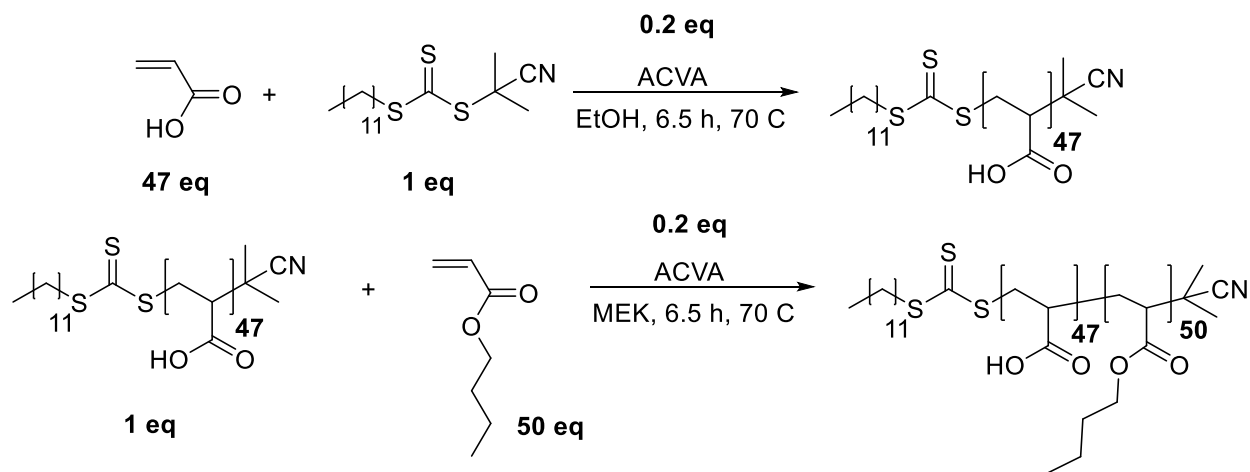


**Figure 8.** Stress versus strain cycles for the multistage PSA with 0.2/0/0 DVB (800D) for set of strains from 10 to 150%, run in order of increasing strain on one sample which failed at 150% strain (black).

There are several possible reasons that this multistage emulsion polymerization approach failed to produce a sacrificial bond network similar to that demonstrated by Ducrot *et al.* in solvent/bulk polymerized acrylics. As mentioned above, the level of DVB used was insufficient to enable any noticeable crosslinking, so it may not have been sufficient to form a primary network to be stretched to form sacrificial bonds. Although the level of ALMA used was sufficient to show evidence of crosslinking, no sample was made in which only the primary network was crosslinked with ALMA. Moreover, as mentioned previously, the reactivity of ALMA may cause it to crosslink only after all of the polymerization stages are completed. These issues could be overcome by using a different level of DVB or a diacrylate crosslinker like the butanediol diacrylate used by Ducrot *et al.* Furthermore, the 30:30:40 primary:secondary:tertiary stage ratio employed in this work may have been insufficient to pre-stretch the primary network. Ducrot *et al.* observed the most effective sacrificial bond behavior when the primary network constituted only 6–10% of the final material (a dual network with 30% first stage did not exhibit sacrificial bond behavior),<sup>8</sup> and many hydrogel dual network tough materials employ 3–5% of primary network.<sup>6</sup> In order to create sacrificial bonds in emulsion particles, it might be necessary to use a much lower proportion of the first stage polymer. Finally, the nature of films generated from emulsion polymer particles may obscure any performance benefit from sacrificial bonds. Because hydrophilic materials in the aqueous phase and on the surface of emulsion polymer particles remain in the film and form weak boundary layers between particles, failure of waterborne PSA materials may occur at particle boundaries rather than within particles. Therefore the toughening effect of sacrificial bond networks in emulsion polymer particles may not offer performance advantage to waterborne PSAs.

## Synthesis and PSA Formulation with Diblock Copolymer to Impart Percolated Network Structure

In a similar vein, the weak interparticle boundary layer in conventional waterborne PSAs inspired us to consider the work of Chenal *et al.* and Gurney *et al.* on constructing strong percolated networks from PAA blocks in the interparticle space.<sup>10, 11, 12</sup> We chose to use a diblock copolymer additive approach similar to that of Gurney *et al.* so that we could explore the effects of this reinforcing architecture on optimized PSAs. We first prepared a BA-based PSA according to a typical optimized process with modifications to use low surfactant and either no acid or 1% AA. We then prepared a PAA-*b*-PBA diblock copolymer according to the process of Gurney *et al.* with slight modifications to allow for quenching to form the PAA-MacroRAFT polymer and re-initiation to form the PBA block (Figure 9). Characterization of the PAA-*b*-PBA diblock copolymer indicated (Table 3) that it was synthesized as expected and in good agreement with prior results. A minor portion of the PAA-MacroRAFT polymer remained unreacted but incomplete conversion of the PAA block was observed previously as well.<sup>12</sup>



**Figure 9.** Synthesis of PAA-*b*-PBA diblock copolymer by RAFT polymerization.

**Table 3.** Characterization of the AA-MacroRAFT polymer and PAA-*b*-PBA diblock copolymer.

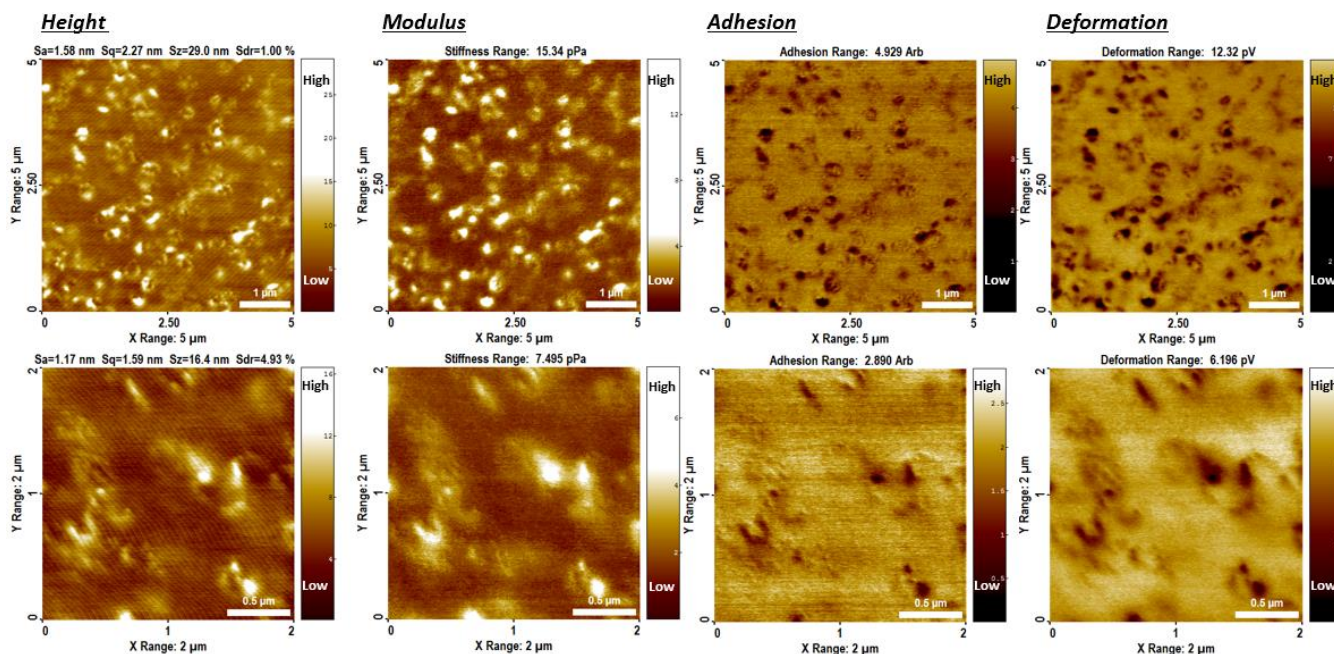
Sample	Target DP (AA/BA)	DP <sup>1</sup> (AA/BA)	M <sub>n</sub> <sup>1</sup>	M <sub>n</sub> <sup>2</sup>	M <sub>w</sub> <sup>2</sup>	PDI <sup>2</sup>	T <sub>g</sub> <sup>3</sup> (°C)
PAA-MacroRAFT	47	49	4072	1589*	2100*	1.32	N.D.
PAA- <i>b</i> -PBA	47/50	49/43	9583	13474	17379	1.29	-35.4,80.6

<sup>1</sup>Obtained from <sup>1</sup>H NMR spectrum integration; <sup>2</sup>Obtained from integration of THF GPC chromatograms.

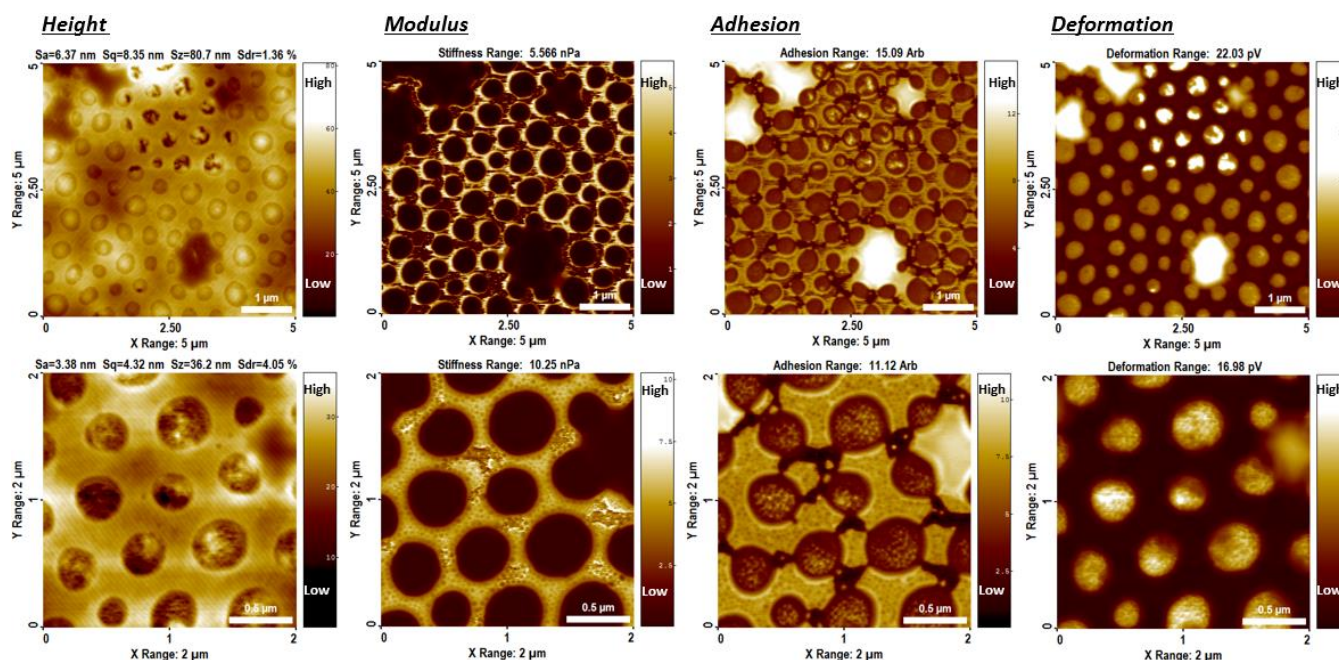
<sup>3</sup>Obtained from DSC. \*PAA showed poor solubility in THF as well poor interaction with the GPC column. This may have led to poor molecular weight estimations. PDI = Polydispersity index.

Nonetheless, although Gurney *et al.* reported that the diblock copolymer could be dissolved in water at 25 wt%, we were unable to dissolve our material in water without the addition of ammonia to neutralize the PAA block. Ultimately an 11.7 wt% solution of the diblock copolymer was obtained at pH 9 for blending with the PSA latexes. This solution was blended with the two low surfactant PSA latexes in order to adsorb the PBA blocks on to the particle surface and the PAA blocks extended into the aqueous phase. Upon drying, the extended PAA blocks are anticipated to form a tough percolated network surrounding the PSA.

**Atomic Force Microscopy (AFM) of PSA/Diblock Copolymer Films Reveals Percolated Network**  
 Surface imaging of height, modulus, adhesion, and deformation on films obtained from PSA/diblock copolymer formulations at pH 8 is consistent with the creation of a percolated network structure. In the PSA with 0% acid alone, little structure is apparent (Figure 10) on the order of the original latex particle diameter (0.5  $\mu\text{m}$ ). This is consistent with nearly complete coalescence of the PBA particles into a uniform film. On the other hand, when diblock copolymer is formulated with this PSA, a percolated network appears which is most clearly seen at 5 wt% diblock copolymer loading (Figure 11).

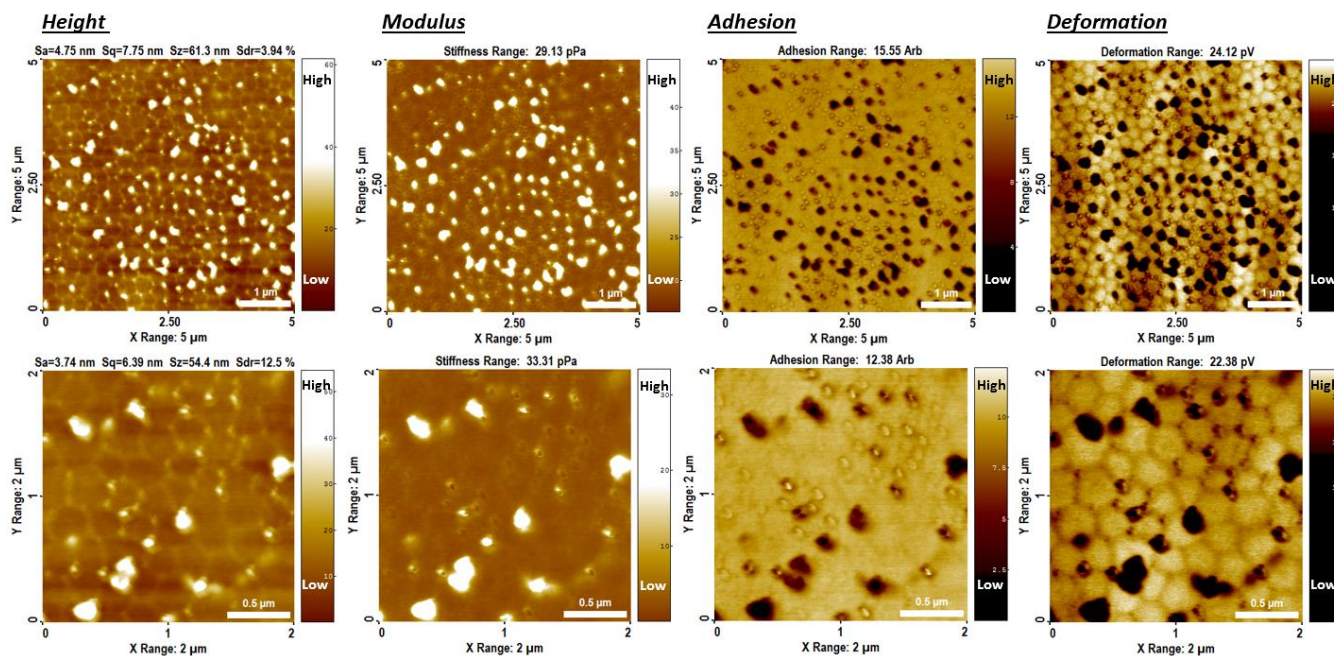


**Figure 10.** Surface AFM of PSA with 0% acid measuring height, modulus, adhesion, and deformation.



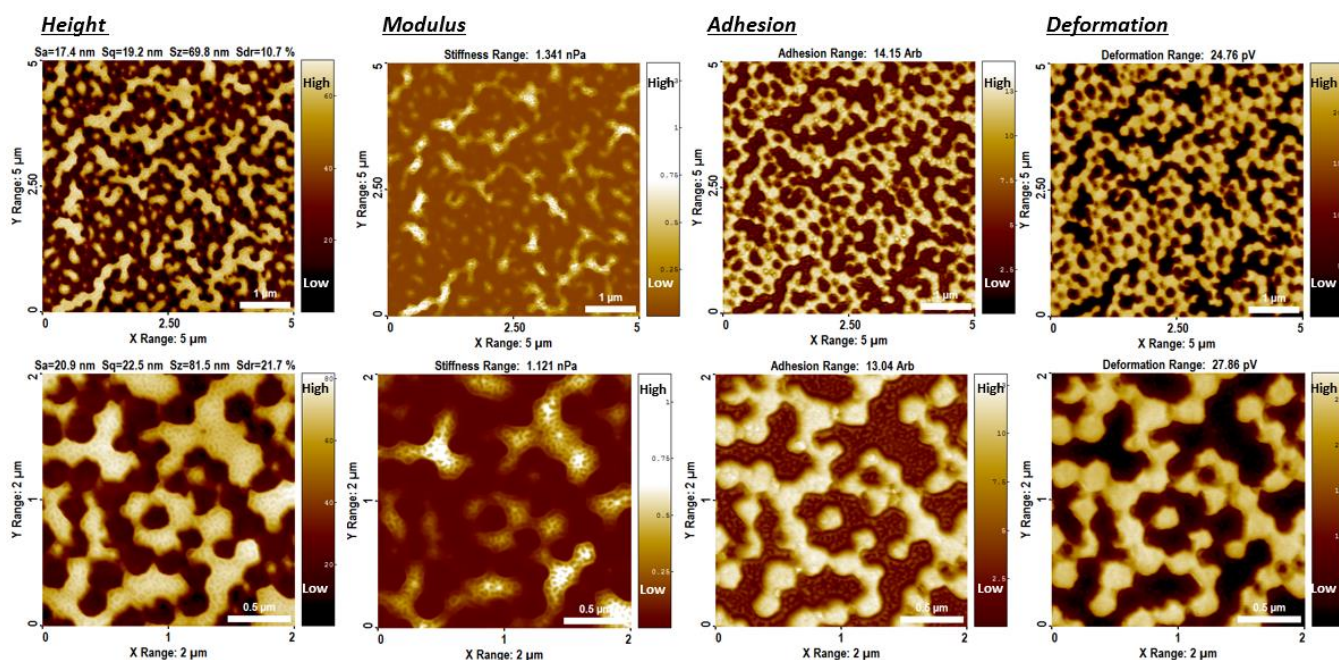
**Figure 11.** Surface AFM of PSA with 0% acid formulated with 5 wt% of PAA-*b*-PBA diblock copolymer measuring height, modulus, adhesion, and deformation.

The dark regions in the modulus map may correspond to the 0.5  $\mu\text{m}$  soft PBA particles, while the stiff percolated phase surrounding the particles corresponds to phase-separated block copolymer. Moreover, the stiffness differences measured are two orders of magnitude greater than for the samples without diblock copolymer ( $\sim 6$  nPa vs.  $\sim 15$  pPA). The adhesion measured on the soft surfaces may be lower than that of the percolated phase due to the soft particles being coated with the PAA chains of the block copolymer. In the modulus and adhesion maps additional microstructure inside each macrophase is apparent (Figure 11, bottom row). Within the percolated phase this microstructure may be due to microphase separation of excess diblock copolymer into micellar structures.



**Figure 12.** Surface AFM of PSA with 1% acid measuring height, modulus, adhesion, and deformation.

The PSA with 1% acid shows a typical latex film structure in which cells on the order of the original latex particle diameter are visible in the height, modulus, and deformation maps (Figure 12). The more clearly defined particle boundaries are likely due to acid moieties on the surface of the particles favoring the formation of a hydrophilic membrane structure on the particle surface which impedes coalescence. With the addition of only 1 wt% diblock copolymer, the structure of the film changes dramatically (Figure 13). A more defined network structure is visible, with a high adhesion and low modulus phase surrounded by a high modulus and low adhesion phase which likely corresponds to diblock copolymer. In addition, the high modulus and low adhesion phase has an internal microstructure which may indicate microphase separation of the diblock copolymer. The appearance of a well-defined network structure in the PSA/diblock copolymer blend at only 1 wt% of diblock copolymer may be due to the additional ordering provided by acid groups on the surface of the PSA particles.



**Figure 13.** Surface AFM of PSA with 1% acid formulated with 1 wt% of PAA-*b*-PBA diblock copolymer measuring height, modulus, adhesion, and deformation.

### Adhesive Properties of PSA/PAA-*b*-PBA Diblock Copolymer Blends

PSA testing was performed on laminate films prepared from PSA/diblock copolymer formulations in order to see whether the percolated network structure imparted by the diblock copolymer enhanced PSA properties. For the experiments shown here, films were prepared by drying the latex at 50°C for 20 minutes because preliminary tests showed that drying at this condition gave similar performance to drying at room temperature for 24 h. When films were dried at 80°C or higher, no adhesion improvement was observed with addition of the diblock copolymer, possibly due to annealing of the PAA block ( $T_g$  80.6°C) during drying.

For the PBA PSA with no acid, formulation with 1–2 wt% of diblock copolymer (BCP) at high pH improved cohesion modestly while also maintaining or increasing adhesion. At pH 8, shear for this PSA improved from 0.3 to 1.1 h while peel and tack increased or stayed the same (Table 4). Formulation with 5% diblock copolymer, however, resulted in lower adhesion and higher shear. Adhesion and cohesion increased simultaneously at pH 10 as well (Table 6), while at pH 5 cohesion increased at the expense of adhesion (Table 5). The different trends at pH 8–10 and at pH 5 may result from ionization of the PAA block at high pH creating a stronger percolated network structure than under low pH conditions which do not fully ionize the PAA block. Although the improvement in adhesion and cohesion with the diblock copolymer is modest, it is notable because these two PSA properties are often difficult to improve simultaneously. In contrast, the PSA with 1% acid had the highest adhesion without the diblock copolymer additive (Table 4), although its shear improved upon addition of the diblock copolymer in line with the typical tradeoff between cohesion and adhesion. Moreover, the overall balance of adhesion and cohesion of the 1% acid PSA was superior to that of any of the diblock copolymer formulations of the PSA with no acid. This indicates that although the diblock copolymer formed a percolated network with the no acid PSA and improved its PSA properties, the percolated architecture still did not afford superior properties in comparison with more conventional waterborne PSAs in which acid moieties are incorporated by copolymerization.

**Table 4.** PSA Results for Laminates Prepared from Formulations at pH 8

Formulation	90° SS Peel (N/in)	SS Loop Tack (N/in)	90° HDPE Peel (N/in)	HDPE Loop Tack (N/in)	SS Shear (h)
0%AA PSA	0.9 (0.1) A	4 (1) A	1.4 (0.1) A	3 (2) A	0.3 (0.1) C
0%AA PSA + 1% BCP	2.4 (0.5) A	4 (1) A	1.0 (0.4) A	4 (1) A	0.8 (0.1) C
0%AA PSA + 2% BCP	1.7 (0.3) A	6.0 (0.3) A	0.9 (0.6) A	3.2 (0.5) A	1.1 (0.1) C
0%AA PSA + 5% BCP	1.2 (0.7) A	2.6 (0.1) A	0.3 (0.1) A	1.1 (0.9) A	3 (2) C
1%AA PSA	2.9 (0.3) A	6.0 (0.8) A	1.5 (0.3) A	3.6 (0.5) A	18 (2) C
1%AA PSA + 1% BCP	1.6 (0.2) A	4.3 (0.5) A	0.8 (0.3) A	2 (1) A	33 (3) C
1%AA PSA + 2 % BCP	1.2 (0.3) A	2.7 (0.7) A	0.5 (0.3) A	1.0 (0.3) A	36 (1) C
1%AA PSA + 5 % BCP	1.9 (0.2) A	2 (1) A	0.4 (0.1) A	0.5 (0.3) A	44 (4) C

All peel tests performed after 20 minute dwell. Standard deviation shown in parentheses.

**Table 5.** PSA Results for Laminates Prepared from Formulations at pH 5

Formulation	90° SS Peel (N/in)	SS Loop Tack (N/in)	90° HDPE Peel (N/in)	HDPE Loop Tack (N/in)	SS Shear (h)
0%AA PSA	1.9 (0.4) A	8.5 (0.9) A	3 (1) A	5.3 (0.7) A	0.5 (0) C
0%AA PSA + 1% BCP	4 (2) A	7.8 (0.3) A	0.8 (0.2) A	4.6 (0.4) A	0.7 (0.1) C
0%AA PSA + 2% BCP	3.1 (0.6) A	3.8 (0.1) A	0.5 (0.2) A	3.4 (0.2) A	2.6 (0.1) C

All peel tests performed after 20 minute dwell. Standard deviation shown in parentheses.

**Table 6.** PSA Results for Laminates Prepared from Formulations at pH 10

Formulation	90° SS Peel (N/in)	SS Loop Tack (N/in)	90° HDPE Peel (N/in)	HDPE Loop Tack (N/in)	SS Shear (h)
0%AA PSA	3.7 (0.3) A	7.8 (0.8) A	2.4 (0.4) A	5.5 (0.4) A	0.5 (0) C
0%AA PSA + 1% BCP	4.5 (0.1) A	6.1 (0.3) A	0.9 (0.1) A	5.0 (0.7) A	0.9 (0) C
0%AA PSA + 2% BCP	4.4 (0.2) A	6.7 (0.8) A	1.4 (0.8) A	5.3 (0.7) A	1.2 (0) C

All peel tests performed after 20 minute dwell. Standard deviation shown in parentheses.

## Conclusions

Hierarchical structures such as sacrificial bonding and percolated networks inspired by nature have previously been shown to impart superior mechanical properties to polymeric materials. However, using these concepts to improve upon highly optimized products such as waterborne PSAs remains challenging. An attempt to design a sacrificial bond network into PSA particles resulted in neither superior PSA properties nor the rheological signatures of sacrificial bonds, likely due to subtle factors affecting the formation of a crosslinked network or the weak boundary layers remaining between particles in the PSA film. Formulation of a PSA with no acid with a PAA-*b*-PBA diblock copolymer engendered a percolated network structure visible by AFM which resulted in a modest simultaneous improvement in adhesion and cohesion. Nonetheless, the PSA properties obtained were inferior to those of a similar PSA with copolymerized acrylic acid. Further effort is needed to understand how to design superior PSAs based on hierarchical architectures.



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