

# Influence of Polymer Microstructure on the Performance of Post-Treated Latex-Based Pressure Sensitive Adhesives

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Received 1 April 2011; accepted 19 May 2011

DOI 10.1002/app.34921

Published online 4 October 2011 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** Latex-based butyl acrylate (BA)/acrylic acid (AA)/2-hydroxyethyl methacrylate (HEMA) pressure sensitive adhesive (PSA) films with various microstructures were heated to improve their performance. The treated PSA films showed significantly better performance than original latex-based PSA films with similar polymer microstructures. The effect of the heat treatment depended on the polymer microstructure of the untreated PSA films (or corresponding lattices). Decreasing the amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ) in gel-free untreated PSA films, or both very small (i.e.,  $M_x < 2M_e$ ) and very large sol polymers (i.e.,  $M_x > 20M_e$ ) in gel-containing

untreated PSA films led to treated PSA films with significantly better performance. (Note:  $M_e$  is the molecular weight between two adjacent entanglement points in a polymer material.) In addition, simultaneously increasing the sol polymer molecular weight ( $M_w$ ) as well as the size of the chain segments between two adjacent cross-linking points ( $M_c$ ) of the gel polymer in the original PSAs resulted in treated PSA films with better performance. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 349–364, 2012

**Key words:** emulsion polymerization; adhesives; pressure-sensitive adhesives; microstructure; post-treatment

## INTRODUCTION

Pressure sensitive adhesives (PSAs) are viscoelastic materials. They can adhere to a substrate even if only a very small force is exerted upon them. PSA performance is generally evaluated by tack, peel strength, and shear strength. Tack measures how well a PSA can bond to a substrate under very short contact time and very small contact force. Peel strength evaluates how strong a PSA can bond to a substrate by peeling it off the substrate. Shear strength characterizes its capability to resist deformation under shear force. In general, an increase in shear strength corresponds to a decrease in tack and peel strength. The reason is that to increase shear strength, the cohesive strength of the PSA must be improved; however, this will lower the PSA's capability to deform and flow, and accordingly, the PSA's capability to wet and adhere to the substrate.

According to their method of production, PSAs can be classified into three categories: solvent-based, hot melt, and water-based PSAs. Solvent-based PSA films are made by casting a polymer solution, hot melt PSAs by casting melt polymers, and water-based PSAs by casting lattices generated via emulsion or suspension polymerization. It is well known

that solvent-based PSAs tend to have much better performance than latex-based PSAs (e.g., much larger shear strength at similar tack and peel strength levels). This is because the gel network is continuous in solvent-based PSAs but discontinuous in latex-based PSAs.<sup>1</sup> Due to their better performance, solvent-based PSAs are widely used in some applications where large shear strengths are needed.

Since the production and use of latex-based PSAs is more environmentally friendly than that of solvent-based PSAs, significant effort has been made to improve the performance of latex-based PSAs so that they can replace their solvent-based counterparts in some applications. The commonly used method for improving the performance of latex-based PSAs includes the following steps: (1) Production of lattices with functional groups that can react either with each other, or with the functional groups of a water-soluble cross-linker; (2) making PSA films using either only the latex or a mixture of the latex and a water-soluble cross-linker; and (3) post-treating these PSA films to encourage the reaction of the functional groups and thus transform the discrete gel into a continuous gel structure. In the past, most of these efforts were focused on the optimization of the functional groups to simplify the post-treatment process.<sup>2–8</sup> The performance of the post-treated PSA is also related to the polymer microstructure of the original latex-based PSA (or corresponding lattices). To our knowledge, only two such studies have been reported.<sup>1,9</sup> In these two publications, Tobing et al.<sup>1,9</sup>

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studied the influence of  $M_w$  (weight-average molecular weight of sol polymer) and  $M_c$  (molecular weight between two adjacent cross-link points) of the gel polymer in the original latex-based PSAs on the performance of treated PSAs. It was found that for gel-free latex-based PSAs, if  $M_w$  was larger than  $2M_e$ , then a continuous gel network could form in its corresponding treated PSAs.  $M_e$  is the molecular weight between two adjacent entanglement points in a polymer material. As for gel-containing PSAs, if they had  $M_w$  larger than  $2M_e$  but smaller or close to  $20M_e$  as well as  $M_c$  larger than  $M_e$ , then their discrete microgels could become a continuous gel network by post-treatment. Under the above two conditions, the treated PSAs showed significantly larger shear strength than the untreated PSAs with similar polymer microstructure. According to Tobing and Klein's criteria, many gel-free lattices have  $M_w > 2M_e$ , and many gel-containing lattices have  $M_c$  larger or close to  $M_e$  as well as  $M_w > 2M_e$  but smaller or close to  $20M_e$ . The question becomes, if choosing from two lattices that meet these criteria, which one can generate post-treated PSA films with better performance?

This study attempts to answer this question. More specifically, by optimizing the polymer properties of the original PSAs, we attempt to improve the performance of post-treated latex-based PSA films. First, a series of lattices that meet Tobing and Klein's criteria were produced. Next, the resulting PSA films were heated to study which latex polymer properties would lead to post-heated PSA films with better performance. In addition, since  $M_w$ , which was the factor studied by Tobing et al.,<sup>1,9</sup> is only an average number and cannot reflect the entire molecular weight distribution of sol polymers, the influence of the amount of very small sol polymers and very large sol polymers on PSA performance was studied. Moreover, similar gel content PSAs with different  $M_c$  and  $M_w$  were used to study if simultaneously increasing  $M_c$  and  $M_w$  could lead to the formation of a more perfect gel network and larger shear strengths for the treated PSAs. Throughout this article, we refer to a "perfect gel network" as one that is continuous with only a small variance in the molecular weight between two adjacent cross-linking points. In other words, we can say that a "perfect gel network" has evenly distributed cross-linking points and therefore less weak points in its structure.

## EXPERIMENTAL

### Materials

Butyl acrylate (BA), acrylic acid (AA), 2-hydroxyethyl methacrylate (HEMA), and methyl methacrylate (MMA) monomers, allyl methacrylate (AMA) cross-linker, n-dodecyl mercaptan (NDM) chain transfer

**TABLE I**  
Polymerization Formulations for Runs 1–7

Ingredients	Initial charge (g)	Feeding (g)	
		Monomer emulsion	Initiator solution
H <sub>2</sub> O	202/15 <sup>a</sup>	89	90
KPS	0.4	–	0.90
BA	11.58	324.48	–
AA	–	6.76	–
HEMA	–	6.76	–
MMA	0.42	–	–
NDM (CTA)	–	0–0.4 phm <sup>b</sup>	–
AMA (cross-linker)	–	0–0.2 phm <sup>b</sup>	–
SDS	0.45	4.25	–
NaHCO <sub>3</sub>	0.05	–	–

<sup>a</sup> Water used for initiator solution in seed production stage.

<sup>b</sup> phm = parts per hundred parts monomer.

agent (CTA), sodium dodecyl sulfate (SDS) surfactant, sodium bicarbonate (NaHCO<sub>3</sub>) buffer, potassium persulfate (KPS) initiator, and hydroquinone (HQ) inhibitor were all obtained from Sigma Aldrich and were used as supplied. All the above materials were reagent grade except HEMA, which had a purity of 97 wt %. Distilled deionized (DDI) water was used throughout the study. Ammonia (30 wt % in H<sub>2</sub>O for pH control) was obtained from British Drug House, Mississauga, Ontario, Canada. All solvents used in the polymer characterization such as tetrahydrofuran (THF, HPLC grade, EMD Chemicals, Gibbstown, New Jersey, USA), toluene (99.8%, Fisher Scientific, Ottawa, Ontario, Canada), and diiodomethane (99%, Sigma-Aldrich, Oakville, Ontario Canada) were also used as supplied by the manufacturer. Nitrogen gas (Linde Canada, Ottawa, Ontario, Canada) was used to purge the reactor. Polytetrafluoroethylene (PTFE) porous membranes with pore size of 0.2 μm, for use in gel content measurements, were purchased from Cole-Parmer Canada, Montreal, Quebec, Canada.

### Latex preparation

All the BA/AA/HEMA (weight ratio: 96/2/2) lattices used for making PSA films were produced via a starved seeded semibatch emulsion polymerization approach. The polymerization process included three stages: a short batch stage to make seed lattices, a long feeding stage to further grow the latex particles, and a short cook stage to fully react the remaining monomers in the lattices. The general polymerization formulation is shown in Table I. To start the polymerization, all the initial charge except for the initiator solution and monomers was added to a one-liter Mettler-Toledo LabMax<sup>TM</sup> reactor at room temperature. The stirring speed was maintained at 250 rpm throughout the polymerization

process. The reactor temperature was then increased to 70°C within 30 min, at which point the monomer mixture and initiator solution were added. The temperature was immediately raised to 75°C within 5 min and was maintained at 75°C for 10 min for the seed latex production stage. Next, the monomer emulsion and initiator solution (see Table I) were fed to the reactor using two separate metering pumps at constant rates and feeding times of 2.5 and 3 h, respectively. At the completion of the feed stage, the polymerization was continued for an additional 50 min to react the remaining monomers (i.e., the cook stage). The latex was then cooled to below 30°C. After polymerization, HQ was added to the latex to stop the reaction. Ammonia and DDI-water were added to adjust the pH to  $\sim 5.5$  and a solids content of  $\sim 45$  wt %. The microstructure of the latex polymers was controlled by varying the amount of CTA and cross-linker used during the feeding stage of the polymerization process.

### Preparation of original and post-treated PSA films

To prepare the original PSA films, two steps were taken. First, lattices were coated on a 50- $\mu\text{m}$  thick Mylar sheet with a #30 Meyer rod to make PSA films with thicknesses of  $\sim 33$   $\mu\text{m}$ . Then, the films were dried and conditioned (24 h at 23°C and relative humidity of 50%) before being tested. To prepare the post-treated PSA films, the conditioned films were heated via two steps: (1) heating at 90°C for 10 min to remove the remaining water in the PSAs; (2) heating at a higher temperature (e.g., 120 or 126°C) to react the carboxyl and hydroxyl groups from AA and HEMA units. These two temperatures were chosen because it was found that at lower temperatures (e.g., 100°C) the reaction was very slow, while at higher temperatures (e.g., 140°C) visible shrinkage of the backing material of the PSA film (i.e., Mylar sheet) was observed. The post-treated PSA films were also conditioned (24 h at 23°C and relative humidity of 50%) before testing.

### Characterization methods

A contact angle method was used to measure the surface tension of the PSA films with VCA Optima contact angle equipment from AST Products. DDI water and diiodomethane were used as the testing liquids with known surface tensions.

The PSA film surfaces were imaged by atomic force microscopy (AFM) in tapping mode using a Multimode Scanning Probe Microscope (Veeco Instruments) and silicon cantilevers (Vistaprobes from NanoScience Instruments). The tip of the cantilever had a pyramidal geometry and the tip radius was 10 nm. The cantilevers had a resonant frequency

of 300 kHz with a spring constant of 40N/m. Height and phase images were taken in air at ambient temperature. The scan speed was 0.9 Hz and the scanned area was about 5  $\mu\text{m} \times 5$   $\mu\text{m}$ .

The detailed testing procedures for gel content,  $M_c$ ,  $M_w$ , and  $M_e$  measurement were described previously.<sup>10</sup> It is worth noting that the swelling method<sup>1</sup> provided  $M_c$  results with very small variability. The  $M_e$  values were estimated using a plasticizer model with very consistent results which have compared well in the past with dynamic mechanical analysis.<sup>11</sup>

Another important molecular weight measurement used in our discussions is that referred to as  $M_x$ . We use  $M_x$  to denote the molecular weight of individual polymer chains as opposed to the weight-average molecular weight of all chains,  $M_w$ .  $M_x$  was calculated from the sol polymer injected into a gel permeation chromatography system. The molecular weights were estimated using the universal calibration technique with monodisperse polystyrene standards and Mark-Houwink parameters weighted on the basis of the copolymer composition.  $M_x$  is related to both  $M_n$  and  $M_w$  by the following equations, where  $N_x$  refers to the number of chains with molecular weight  $M_x$ :

$$M_n = \frac{\sum M_x N_x}{\sum N_x} \quad (1)$$

$$M_w = \frac{\sum M_x^2 N_x}{\sum M_x N_x} \quad (2)$$

The tack, peel strength, and shear strength were measured according to the Pressure Sensitive Tape Council standards PSTC-6, PSTC-1 and PSATC-7, respectively.<sup>12</sup> Details of the testing procedures were also provided previously.<sup>13</sup> In this study, the shear strength was measured using two contact areas: 1 in.  $\times$  1 in. and [1/2]";  $\times$  [1/2]"; because it was found that with a contact area of 1 in.  $\times$  1 in., most of the heated PSAs showed shear strengths too large to be measured within a reasonable time period (e.g., >1 month).

## RESULTS AND DISCUSSION

The goal of this study was to improve the performance of post-treated latex-based PSAs by optimizing the polymer microstructure of the original PSAs. For this purpose, a series of BA/AA/HEMA lattices with a variety of polymer microstructures was produced for the preparation of PSA films. The polymer properties of these lattices are shown in Table II. These lattices were produced via two different techniques: one by varying the amount of CTA in the absence of cross-linker; the other by using CTA and cross-linker simultaneously. From Table II, one can see that some of these lattices had very interesting



**TABLE II**  
**Polymer Properties of BA/AA/HEMA (Weight Ratio: 96/2/2) Lattices**

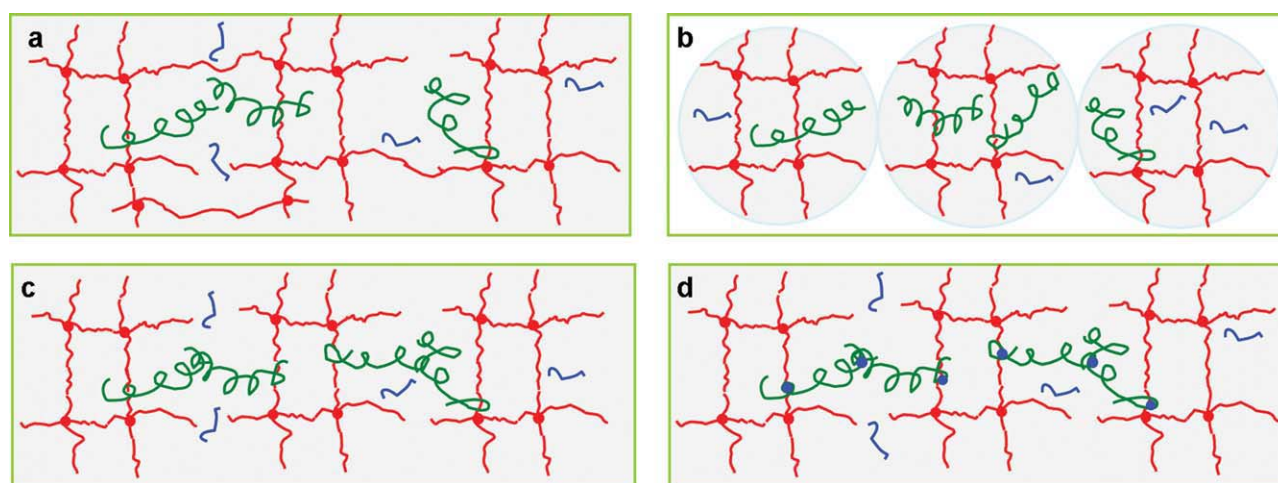
Latex ID <sup>a</sup>	Gel content (wt %)	$M_w$	$M_n$	$M_c$	$M_e$
		( $\times 10^{-3}$ g/mol)			
1	0	252	48	–	26
2	13	470	66	–	22
3	36	656	78	–	22
4	51	443	105	82	21
5	75	217	70	59	21
6	49	113	28	38	27
7	74	87	42	20	23

<sup>a</sup> Lattices 1–5 were generated by varying the amount of CTA in the absence of cross-linker while lattices 6 and 7 were produced using both CTA and cross-linker.<sup>10</sup>

microstructures (e.g., similar gel content but different  $M_c$  and  $M_w$ ). The reasons for the formation of such unique latex polymer microstructures were provided previously.<sup>10</sup> It should be noted that the PSA films used in this study were the ones identified in a previous study<sup>10</sup> using a “B,” which referred to a latex with a pH of 5.5. In this study, the post-treated PSA films were named after their respective latex ID as well as the heating condition. For example, PSA 5-126/11 refers to the PSA film cast from latex 5 heated at 126°C for 11 min.

A schematic representation of the latex-based PSA film formation process as well as the polymer microstructures of the original and treated PSA films is shown in Figure 1. The polymer microstructure of a solvent-based PSA film is also provided in Figure 1 for comparison. A solvent-based PSA film has a con-

tinuous gel structure [see Fig. 1(a)]. Latex-based PSA films are formed by casting the lattices [see Fig. 1(b)]. The water in the lattices will evaporate and at the same time, some sol polymers of one latex particle will diffuse across the particle boundary. Then, if the latex polymer microstructure is appropriate (i.e.,  $M_w > 2M_e$  and  $M_c \geq M_e$ ), the diffused sol polymers will entangle with the sol polymer or gel polymers from another particle.<sup>1,9</sup> Meanwhile, the latex particles will deform, the particle boundary will disappear gradually, and finally, a latex-based PSA film will form [see Fig. 1(c)]. From Figure 1(c), one can see that in latex-based PSA films, the gel is discrete, and the small microgel polymers are connected together strictly by sol polymer chain entanglement. Actually, this is the best scenario, and in some cases, the microgels do not entangle. The discrete gel structure is often the cause for the lower shear strength of latex-based PSA films, compared with that of solvent-based PSA films. If the latex-based PSA polymer contains certain functional groups, then by post-treating the PSA film, some entanglement points can be transformed into cross-linking points [see Fig. 1(d)]. As a result, the discrete gel structure will be turned into a more continuous gel network and the shear strength will be greatly improved. Meanwhile, from Figure 1(d), one can see that the continuous gel structure in the treated PSAs is not necessarily uniform. Weak points often exist around the edge of the original microgels in the treated PSAs if the microgels were not originally connected via a sufficient number of cross-linking points. The presence of these weak points can lead to a decrease in the cohesive strength of the treated PSA films and thus,



**Figure 1** Schematic representation of the polymer microstructures of PSA films and latices, as well as the latex-based PSA film formation process. (a) Solvent-based PSA film, (b) Latex particles, (c) Latex-based PSA film, and (d) Post-treated latex-based PSA film (Note: In images a–d, the grids and associated solid dots represent the gel polymers and their cross-link points, respectively. The long curled lines represent sol polymers with  $M_x > 2M_e$ ; and the short lines refer to the small sol polymers incapable of entanglement with other sol polymers or gel polymers. The solid dots in image d linking the grids and sol polymers represent newly formed cross-linking points during the post-treatment process for the latex-based PSA films). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

**TABLE III**  
Polymer Microstructures of the Original and Heated PSA 1

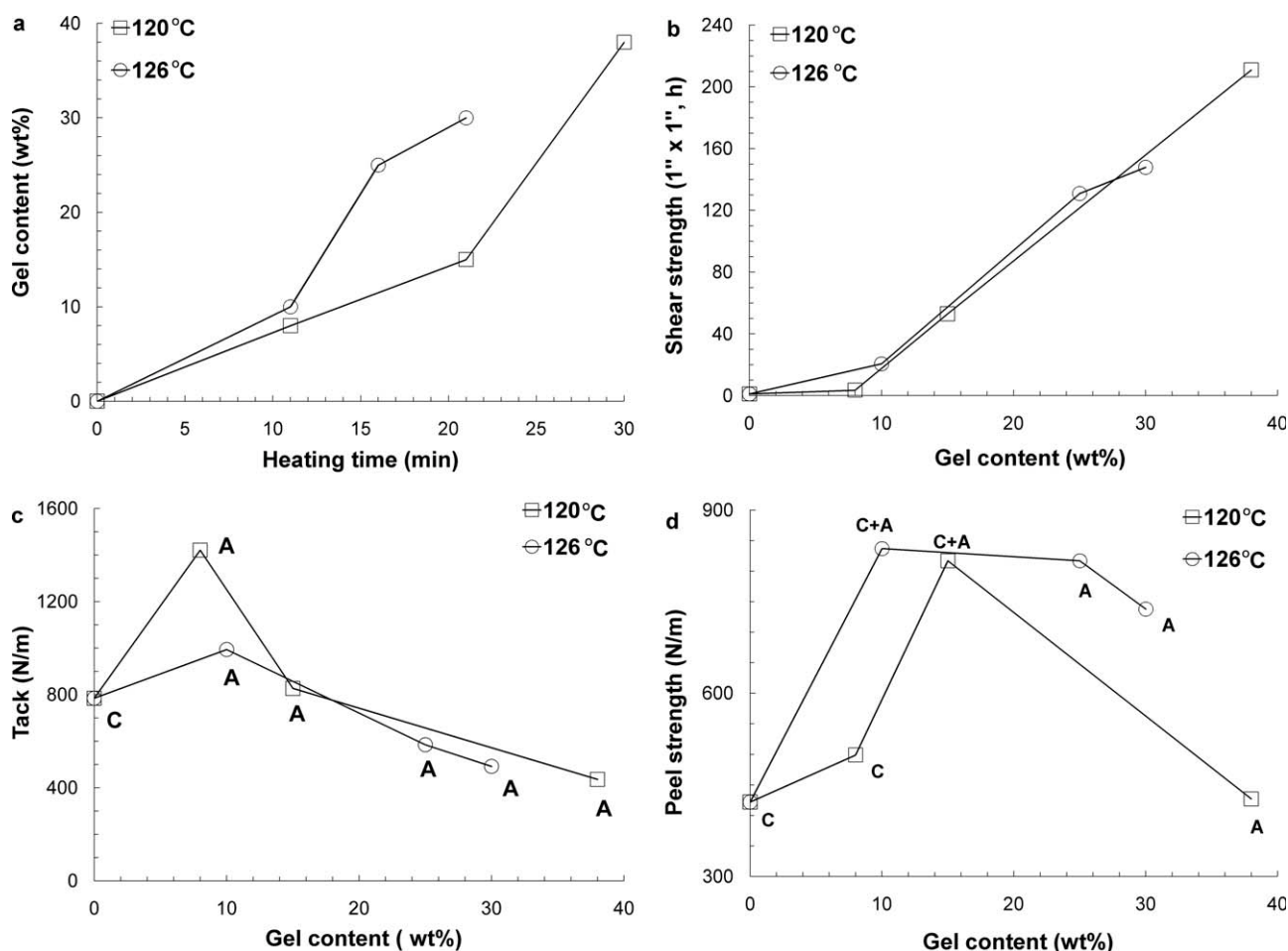
PSA ID	Gel content	$M_w$	$M_n$	MWD
	(wt %)			
1	0	252	48	5.2
1-120/11	8	532	84	6.3
1-120/21	15	643	88	7.3
1-120/30	38	425	75	5.7
1-126/11	10	534	101	5.3
1-126/16	25	424	100	4.2
1-126/21	30	382	86	4.4

a decrease in shear strength. To improve the performance of the treated PSA films, these weak points in their continuous gel network must be eliminated. The way to achieve this is to optimize the polymer properties of the untreated PSA films, to ensure that the microgels will be very well entangled and consequently, in the treated PSA films, the original microgels will be connected via a sufficient number of cross-linking points.

### Polymer microstructure and performance changes during the post-treatment process of gel-free PSA 1

Gel-free PSA 1 was heated to study the polymer microstructure and performance changes during the heating process for PSAs with similar polymer microstructures. Two temperatures (i.e., 120 and 126°C) were used to heat the PSA. The polymer microstructures and performance of the original and heated PSAs are shown in Table III, and Figure 2, respectively.

From Figure 2(a), one can see that at a given heating temperature, the gel content increased with heating time (e.g., from 0 to 38 wt % at 120°C). From Table III, one can see that with the increase in gel content,  $M_w$  first increased to a maximum at a very small gel content (i.e., 15 wt % at 120°C) and then decreased. This trend in  $M_w$  with increasing gel content observed with the heated PSAs was the same as that observed with the original PSAs (i.e., 1–5) shown in Table II. Through the reaction between the carboxyl and hydroxyl groups from the AA and HEMA units, two or more polymer chains could be



**Figure 2** (a) Gel content change with heating time during the heating process of PSA 1; (b–d) PSA performance changes with gel content for the original and heated PSA 1 (Note: In the tack and peel strength figures, [Figure 2(c,d)] “C”, “A,” and “C + A” refer to cohesive failure, adhesive failure, and coexisting cohesive and adhesive failure, respectively).

**TABLE IV**  
**Polymer Properties of PSA Films 3, 4, 1-126/16,**  
**and 1-120/30**

PSA ID	Gel content (wt %)	$M_w$	$M_n$	$M_c$	$M_e$
		( $\times 10^{-3}$ g/mol)			
3	36	656	78	–	22
4	51	443	105	82	21
1-126/16	25	424	100	–	–
1-120/30	38	425	75	–	–

chemically bonded and form one larger polymer chain. If the resulting polymer was sufficiently large, it would become gel polymer; otherwise, it would remain sol polymer. If the heating time was not sufficient, most of the sol polymers grew into larger sol polymers while a small amount became gel polymers. Hence,  $M_w$  increased with gel content. Further heating resulted in the formation of a significant amount of gel polymers in the treated PSAs and an increase in gel content. These gel polymers in the treated PSAs were mainly from the larger sol polymers in the untreated PSAs, as they had more functional groups for reaction and consequently further growth. With the transformation of a significant amount of larger sol polymers into gel polymers, the average size of the sol polymers ( $M_w$ ) decreased.

Figures 2(b–d) show that shear strength increased with gel content while tack and peel strength displayed maxima. This PSA performance trend with increasing gel content is very similar to that previously observed with the unheated latex-based PSA films shown in a previous study.<sup>10</sup> With the increase in gel content, the cohesive strength of the PSA films was enhanced, resulting in larger shear strength. Meanwhile, larger cohesive strength decreased the PSAs' deformability and flow ability, and led to less wetting of the PSA films on the substrate during the bonding process. In addition, the higher gel content lowered the PSA's capability for elongation<sup>14</sup> and consequently, the PSAs with a larger gel content could experience a much smaller strain during the debonding process<sup>15,16</sup> compared with those with a lower gel content. Thus, the PSAs with larger gel contents dissipated a smaller amount of energy during the debonding process. Less wetting as well as less dissipated energy led to a general decrease in tack and peel strength with increasing gel content. The special case of tack and peel strength increases with gel content observed at very low gel contents (e.g., from 0 to 15 wt %) can be explained as follows: (1) due to the very small gel content, the negative effect of gel on decreasing the PSAs' elongation capability was negligible; (2) when the gel content was low, the  $M_w$  increased with gel content, as discussed earlier. The increase in  $M_w$  endowed the

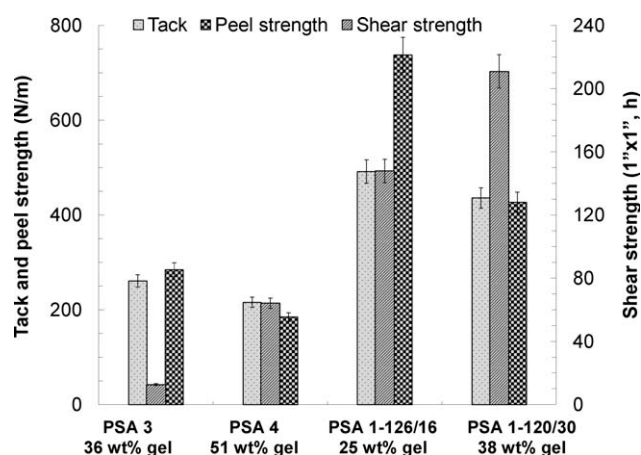
higher gel content PSAs with larger elongation capability compared to the lower gel content PSAs. Consequently, the larger gel content PSAs could have experienced larger strain and dissipated a larger amount of energy during the debonding process. For these very low gel content PSAs, the positive effect of a larger amount of dissipated energy on tack and peel strength might have counterbalanced the negative effect of less wetting, hence the tack and peel strength increased with gel content.

#### Comparison of the performance of post-treated PSAs generated from PSA 1 to those of original latex-based PSAs 3 and 4

The post-treated PSA films (i.e., 1-126/16 and 1-120/30) were compared with original PSA films 3 and 4 with respect to their polymer microstructure and performance. The polymer properties and performance of these PSAs are shown in Table IV and Figure 3, respectively.

From Table IV and Figure 3, one can see that at a lower gel content (i.e., 25 wt %), PSA 1-126/16 showed significantly larger shear strength as well as larger tack and peel strength than PSAs 3 and 4 with higher gel contents (i.e., 3: 36 wt %, 4: 51 wt %). The better performance of the treated PSA was related to its unique microstructure. Since PSA 1 was gel-free and had  $M_w > 2M_e$  (see Table II), the gel network in its corresponding treated PSAs should be continuous, while the gels in PSAs 3 and 4 were discrete. Hence, PSA 1-126/16 showed significantly larger shear strength than PSAs 3 and 4, despite its lower gel content.

The higher tack and peel strength of PSA 1-126/16 can also be explained. At significantly lower gel content, PSA 1-126/16 should have much larger deformability and flow ability, compared with PSAs 3 and 4. Hence, it could wet the substrate better during



**Figure 3** Performance of PSA films 3, 4, 1-126/16, and 1-120/30.



**TABLE V**  
**Polymer Properties of the PSA 1 and 2 as Well as Their Heated Counterparts**

PSA ID	Gel content (wt %)	$M_w$	$M_n$	$M_e$	$x^*$
		( $\times 10^{-3}$ g/mol)			(wt %)
1	0	252	48	26	32
1-120/30	38	425	75	–	–
2	12	470	66	22	15
2-126/16	40	394	70	–	–

$x^*$  refers to the weight percentage of the very small sol polymers with  $M_x < 2M_e$  in the total sol polymers. This number was obtained via GPC.0.

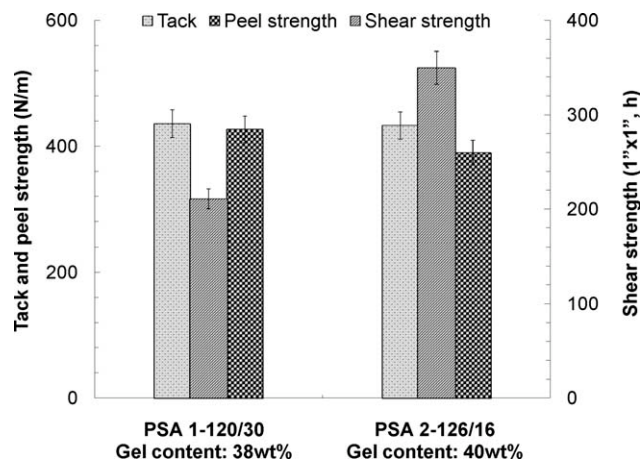
tack and peel strength testing. Meanwhile, due to its lower gel content, it should have much larger elongation capability and accordingly should have dissipated more energy by forming a larger strain during the debonding process of tack and peel strength testing. Both better wetting and a larger amount of dissipated energy contributed to the larger tack and peel strength of PSA 1-126/16.

From Tables IV and Figure 3, one can also see that at similar gel contents (i.e.,  $\sim 36$  wt %), the PSA 1-120/30 showed significantly larger shear strength as well as larger tack and peel strength, compared with PSAs 3 and 4. The larger shear strength was due to its continuous gel structure. The much larger tack and peel strength could be caused by two factors. First, PSA 1-120/30 may have had a loose gel network (larger  $M_e$ ), compared with PSA 3 with similar gel content. Hence, it had larger deformability and could wet the substrate much better. Second, the heated PSA film might have had a much smoother surface, due to the possible flow of PSA polymers during the heating process.

#### Influence of very small sol polymers in the gel-free or low gel content latex-based PSAs on the performance of their treated PSAs

PSAs 1 and 2 were heated to study the influence of very small sol polymer (i.e.,  $M_x < 2M_e$ ) in the original PSAs on the performance of treated PSAs. One should note that here, we use  $M_x$  to denote the molecular weight of individual polymer chains as opposed to the average molecular weight of all chains,  $M_w$ . The polymer properties of these two PSAs and their treated counterparts are shown in Table V. The performance of PSAs 1-120/30 and 2-126/16 is shown in Figure 4.

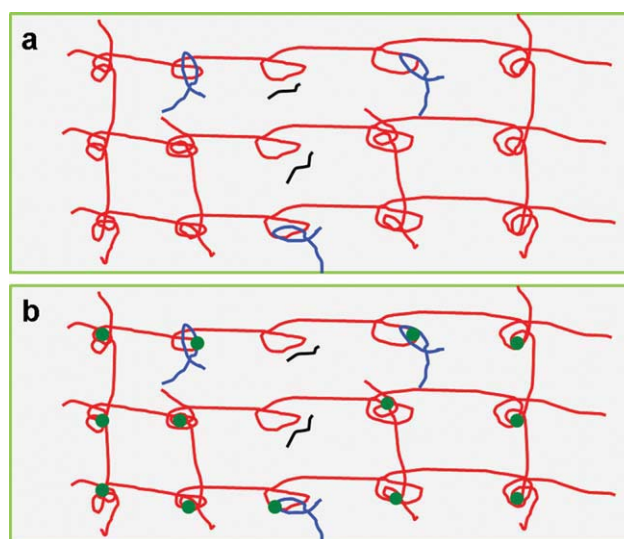
From Table V and Figure 4, one can see that at a similar gel content (i.e.,  $\sim 40$  wt %), PSA 1-120/30 had significantly smaller shear strength but similar tack and slightly higher peel strength, compared with PSA 2-126/16. Considering the close tack and peel strength values, the  $M_e$  should also be similar. Otherwise, these two PSAs would have exhibited a



**Figure 4** Performance of PSA films 1-120/30 and 2-126/16.

significant difference in deformability and wetting capability on the testing panel, resulting in a significant difference in tack and peel strength values. Since PSAs 1-120/30 and 2-126/16 had similar gel contents and very likely, similar  $M_e$ , the significantly smaller shear strength of the former PSA was likely due to its less continuous gel network.

From Table V, one can see that both PSAs 1 and 2 had very low gel contents as well as  $M_w > 2M_e$ . Hence, their respective treated PSAs (i.e., 1-120/30 and 2-126/16) should both have continuous gel networks.<sup>1</sup> Table V also shows that PSA 1 had a much larger amount of very small sol polymers ( $M_x < 2M_e$ ), compared with PSA 2 (i.e., 32 wt % versus 15 wt %). These very small sol polymers could have a very negative effect on the gel network of the treated



**Figure 5** Schematic representation of the polymer microstructures of a latex-based PSA film with very small sol polymer ( $M_x < 2M_e$ ) as well as its post-treated counterpart (a) original PSA film; (b) post-treated PSA film. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE VI**  
**Polymer Properties and Performance of PSAs 5, 7 and Their Heated Counterparts**

PSA ID	Gel content (wt %)	$M_w$	$M_n$	$M_c$	$M_e$
		( $\times 10^3$ kg/mol)			
5	75	217	70	59	21
5-126/11	81	161	78	53	–
7	74	87	42	20	23
7-126/11	79	73	42	22	–
PSA ID	Tack (N/m)	Peel strength (N/m)		Shear strength (h, 1/2" $\times$ 1/2")	
5	176	104		1.10	
5-126/11	280	190		>336 h (2 weeks) <sup>a</sup>	
7	154	87		0.70	
7-126/11	209	118		292.80	

<sup>a</sup> No sign of shear failure was observed after 2 weeks.

PSAs. According to Figure 5, very small sol polymers with  $M_x \geq M_e$  but  $< 2M_e$  only entangled with other polymer chains at one end; while the very small sol polymers with  $M_x < M_e$  cannot entangle with other polymer chains [see Fig. 5(a)]. For example, even if a larger polymer chain formed a loop around a very small sol polymer with  $M_x < M_e$ , they cannot entangle. After treatment, the very small sol polymers with  $M_x \geq M_e$  but  $< 2M_e$  could become branches [see Fig. 5(b)]. Although these branches were part of the gel network, they could not enhance the network's capability to resist deformation. In addition, the presence of a significant amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ) in the original PSA films could cause a very large variance of the chain segments between two adjacent cross-linking points of the gel network in their corresponding post-treated PSAs [see Figs. 5(a,b)]. The formation of such an imperfect gel network would lower the post-treated PSA films' capability to resist deformation, and accordingly, would lead to smaller shear strength for the post-treated PSA films. From the above result and discussion, one can see that increasing the amount of very small sol polymers in very low gel content latex-based PSAs had a significant negative effect on the performance of their treated PSAs.

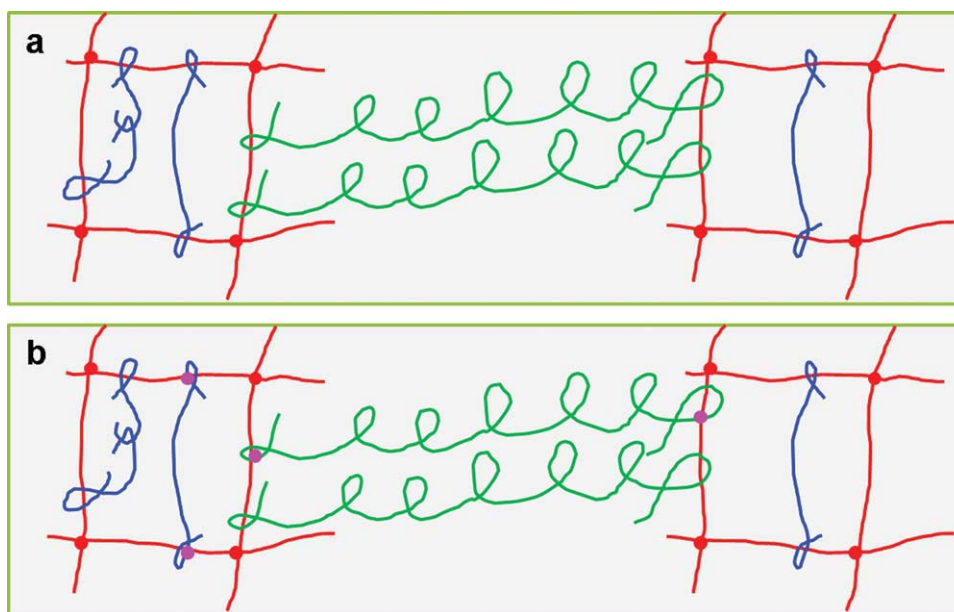
#### Influence of simultaneously increasing the $M_c$ and $M_w$ of latex-based PSAs on the performance of their treated PSAs

PSAs 5 and 7 were post-treated under the same conditions (126°C/11 min) to see if simultaneously increasing the  $M_c$  and  $M_w$  for similar gel content latex-based PSAs would result in better performance for the corresponding treated PSAs. The polymer properties and performance of PSAs 5 and 7 as well as their heated counterparts (i.e., 5-126/11 and 7-126/11) are shown in Table VI.

From Table VI, one can see that PSAs 5 and 7 had similar gel contents ( $\sim 75$  wt %), but the  $M_c$  and  $M_w$  of PSA 5 were much larger than those of PSA 7. In addition, PSA 5 had  $M_c > M_e$  and  $M_w > 2M_e$ , so the microgels in PSA 5 could be entangled by the sol polymers. As for PSA 7, its  $M_w$  was also larger than  $2M_e$  but its  $M_c$  was close to  $M_e$ . However, since  $M_c$  is only an average number of the size of the chain segments between two adjacent cross-linking points, the microgels in PSA 7 might be entangled by the sol polymers. In any case, compared with PSA 7, the microgels in PSA 5 should be better entangled by the sol polymers, due to its larger  $M_c$  and  $M_w$ . This has been confirmed by the larger shear strength of PSA 5 compared to PSA 7 (see Table VI) (Note: Detailed explanations for the differences in polymer microstructure, viscoelastic properties as well as performance between PSA 5 and 7 were provided previously.)<sup>10</sup>

Table VI also shows that PSA 5-126/11 had a larger gel content, smaller  $M_w$  and slightly smaller  $M_c$  compared with PSA 5. A similar polymer microstructure difference was observed by comparing PSA 7-126/11 to PSA 7. The decrease in  $M_w$  with increasing gel content resulted as larger sol polymers in PSAs 5 and 7 were more likely to undergo further growth and thereafter become part of the gel network during the heating process due to their larger size and greater amount of functional groups present. The essentially unchanged  $M_c$  observed after post-treating PSA 5 (i.e.,  $M_c$ : 59 and 53 kg/mol for 5 and 5-126/11, respectively) was unexpected. However, the gel content only increased by a small amount (i.e., 6 wt %) after post-treating PSA 5, hence the  $M_c$  did not change significantly. Also, the  $M_c$  of PSA 5 was  $\sim 3M_e$ , hence some sol polymers were trapped inside the microgels in PSA 5, and some of them also entangled with the microgels [see Fig. 6(a)]. The transformation of this type of entanglement point into a cross-linking point during the heating process would tend to decrease the  $M_c$  (see





**Figure 6** Scheme of the  $M_c$  change during the post-treatment process of PSA 5. (a) Before post-treatment; (b) After post-treatment. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Fig. 6). In contrast, in PSA 5, some sol polymer chains entangled with two adjacent microgels. If these types of entanglement points transformed into cross-linking points during the heating process, the  $M_c$  might tend to increase. The reason is the newly formed chain segment between the two adjacent cross-linking points could be as big as the reacted sol polymers, which had a size much larger than the  $M_c$  of PSA 5 (see Fig. 6). These two contradictory effects on  $M_c$  might have counterbalanced each other, resulting in a negligible change in  $M_c$  after post-treating PSA 5.

Table VI shows that after post-treating PSAs 5 and 7, the shear strength significantly increased, despite a small gel content change. For example, PSA 5 (gel content: 75 wt %) had a shear strength of 1.1 h and PSA 5-126/11 (gel content: 81 wt %) exhibited a shear strength larger than two weeks. This suggests that the discrete gel network had been changed into a continuous gel network after post-treating PSAs 5 and 7. In addition, from Table VI, one can see that at a similar gel content of about 80 wt %, PSA 5-126/11 had significantly larger shear strength, compared with PSA 7-126/11, despite its larger  $M_c$  (looser gel network). Clearly, a more perfect gel network was formed in PSA 5-126/11 compared with PSA 7-126/11. This was due to the fact that the simultaneous increase in the  $M_c$  and  $M_w$  for similar gel content latex-based PSAs could induce more sol polymer entanglements with the microgel and consequently, the connections between the microgels were improved. Accordingly, a more perfect continuous gel network would form in its corresponding treated PSA film, resulting in higher shear strength.

From Table VI, we also observe that after post-treating PSAs 5 and 7, the tack and peel strength were significantly increased. For example, the tack and peel strength were 170 and 104N/m for PSA 5 and, 280 and 190N/m for PSA 5-126/11, respectively. This increase in tack and peel strength with increasing gel content was unexpected, as it was previously found that for BA/AA/HEMA (weight ratio: 96/2/2) PSAs, the tack and peel strength decreased with increasing gel content when the gel content was larger than  $\sim 15$  wt %.<sup>10</sup> It is suspected that the PSA surface tension might have changed after post-treatment, since it is possible to increase PSA films' peel strength by increasing their surface tension and consequently the chemical interaction energy between the surfaces of these PSA films and substrate.<sup>11,17</sup> Hence, the surface tensions were measured for PSAs 5 and 5-126/11. The calculation procedure was according to that of a previous publication by Yang and Chang.<sup>19</sup> The calculation results are shown in Table VII.

From Table VII, one can see that PSA 5-126/11 had a smaller surface tension ( $\gamma_P$ ) compared with PSA 5, and consequently a smaller chemical interaction energy ( $I$ ) between the PSA film and the stainless steel testing panel. Actually, the smaller surface tension of the heated PSA was consistent with the reaction between AA and HEMA during post-treatment. After reaction, the polar carboxyl and hydroxyl groups from AA and HEMA units became nonpolar ester groups and tended to decrease the PSA's surface tension. However, considering the very large change in contact angle with water after post-treatment (i.e., 59 vs. 97 degrees), as well as the

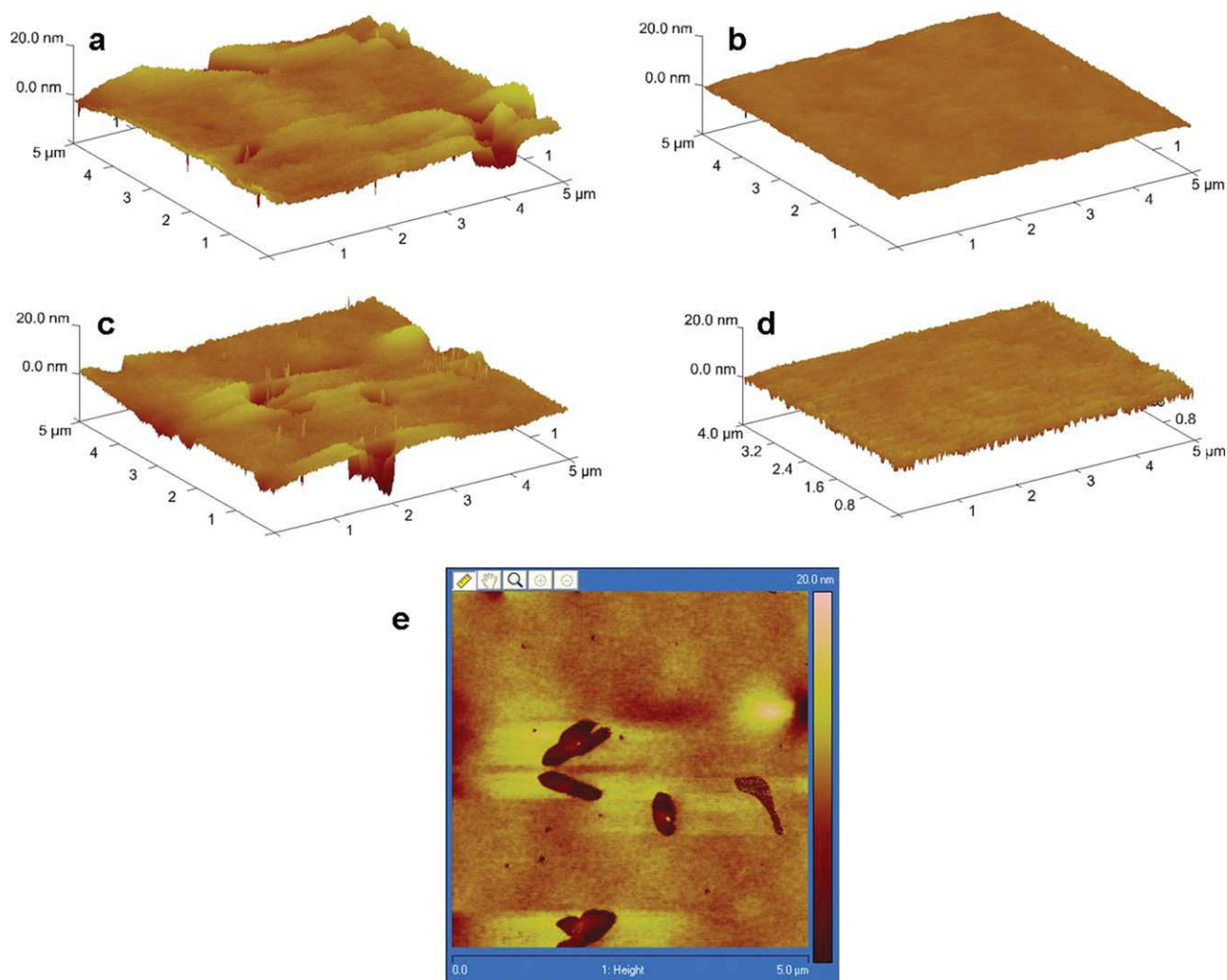
**TABLE VII**  
**Contact Angle Measurement Data for PSA 5 and 5-126/11**

PSA ID	Contact angle (°)		$\gamma^d$	$\gamma^p$	$\gamma$	$I$
	$\theta_1$ (H <sub>2</sub> O)	$\theta_2$ (CH <sub>2</sub> I <sub>2</sub> )				
5	59	72	15	30	45	84
5-126/11	97	71	20	6	26	67

$\gamma_p$ ,  $\gamma_p^d$ , and  $\gamma_p^p$  are the PSAs' surface tension, and the dispersion and polar components of the surface tension.  $I$  is the chemical interaction energy between the surfaces of the PSA film and the stainless steel testing panel.

small amount of reacted AA and HEMA during the heating process, it is suspected that the PSA surface smoothness had changed. Smoother surfaces can lead to larger contact angles. To confirm this, the surfaces of PSAs 5, 7, 5-126/11, and 7-126/11) were characterized via AFM (see Fig. 7).

From Figure 7, one can see that PSA films 5 and 7 had some defects, which were too small to be observed with the naked eye, but were detectable with AFM. These defects may have been caused by the slightly lower viscosity of the lattices, or a very small amount of coagulum, which was too small to be removed from the lattices via filtration. In contrast, PSAs 5-126/11 and 7-126/11 did not present these defects. In addition, the surfaces of the heated PSAs were much smoother than those of the unheated ones. Apparently, the PSA polymer flowed during the heating process, resulting in a smoother surface after post-treatment. Hence the post-treated PSAs showed higher tack and peel strength than their unheated counterparts. Moreover, comparing Figure 7(b,d), one can see that the surface of PSA 5-126/11 was much smoother compared to that of PSA 7-126/11. This might also have contributed to the higher tack and peel strength of the former PSA, in addition to the polymer microstructure



**Figure 7** Surface images of PSA films 5, 7, and their heated counterparts; (a)–(d) are three-dimensional height images (a: 5, b: 5-126/11, c: 7, d: 7-126/11); and e is the two-dimensional image height image of PSA 7). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**TABLE VIII**  
**Polymer Properties and Performance of PSAs 4, 5, 6 and the Heated Counterparts for PSAs 4 and 6**

PSA ID	Gel content (wt %)	$M_w$	$M_n$	$M_c$	$M_e$	$x^{*,b}$
		( $\times 10^3$ kg/mol)			(wt %)	
4	51	443	105	82	21	10
4-126/11	70	216	73	–	–	–
6	49	113	28	38	27	48
6-126/11	63	109	43	–	–	–
5 <sup>a</sup>	75	217	70	59	21	–
PSA ID	Tack (N/m)	Peel strength (N/m)		Shear strength (h, 1/2" $\times$ 1/2")		
4	216	185		0.52		
4-126/11	323	236		11.30		
6	223	203		0.13		
6-126/11	450	270		5.10		
5 <sup>a</sup>	176	104		1.10		

<sup>a</sup> PSA5 was used as the control sample to compare the performance of latex-based PSAs with that of the post-treated PSAs.

<sup>b</sup>  $x^*$  refers to the weight percentage of the sol polymers with  $M_x < 2M_e$  in the total sol polymers.

differences mentioned earlier. The smoother surface of PSA 5-126/11 can be explained. Both PSA 5 and 7 had a very large amount of gel polymer ( $\sim 75$  wt %), hence  $M_c$  should have a significant influence on the polymer expansion and flow during the heating process. PSA 5 had a much looser gel structure ( $M_c = 59$  kg/mol) compared with PSA 7 ( $M_c = 20$  kg/mol), hence the microgel polymer of PSA 5 should have expanded more and thereafter flowed much more during the heating process. As a result, the PSA 5-126/11 presented a smoother surface compared with PSA 7-126/11.

From the above results, one can see that post-treatment can greatly improve the performance of latex-based PSAs. Shear strength can be increased along with tack and peel strength. In addition, simultaneously increasing the  $M_c$  and  $M_w$  for similar gel content latex-based PSAs, could impart better performance of the treated PSAs (e.g., larger shear strength as well as larger tack and peel strength).

#### **Influence of increasing the amount of very small sol polymers in gel-containing latex-based PSAs on the performance of their treated PSAs**

PSAs 4 and 6 were post-treated under the same conditions (126°C/10 min) to study if increasing the amount of very small sol polymer in gel-containing latex-based PSAs (i.e.,  $M_x < 2M_e$ ) could have a significant influence on the treated PSAs. The polymer properties and performance of PSAs 4, 6, 4-126/11, and 6-126/11 are shown in Table VIII.

From Table VIII, one observes that PSAs 4 and 6 both had  $M_w > 2M_e$  and  $M_c > M_e$ . Hence, the microgels could be entangled by the sol polymers in both

PSAs. In addition, PSAs 4 and 6 had similar gel contents, but PSA 4 had a much larger  $M_c$  and  $M_w$  compared with PSA 6. This is similar to the comparison of PSA 5 with 7. Another significant difference between PSA 4 and 6 was that PSA 4 had a much smaller amount of very small sol polymers (i.e.,  $M_x < 2M_e$ , 10 wt % versus 48 wt % of the total sol polymers, see Table VIII). Therefore, PSA 4 should have had a better entanglement between the sol polymers and microgels, compared with PSA 6. This is consistent with the significantly larger shear strength of PSA 4 (i.e., 0.52 h vs. 0.13 h) (Note: The detailed explanations with respect to the different microstructures, viscoelastic properties and performance between PSAs 4 and 6 were provided in a previous study).<sup>10</sup>

Table VIII also shows that after heating, PSAs 4 and 6 showed increases in gel content and decreases in  $M_w$ . Moreover, from Tables VII and V, one can see that after heating under the same conditions (126°C/11 min), PSAs 4 and 6 showed much larger increases in gel content (i.e., 19 wt % and 14 wt %), compared with PSAs 5 and 7 (i.e., 6 and 5 wt %). This occurred because PSAs 4 and 6 had more sol polymers available for further growth into gel polymers. In addition, from Table VIII, one can see that after heating PSAs 4 and 6, the films showed a significant increase not only in shear strength but also tack and peel strength. Moreover, from Table VIII, one can see that PSAs (4-126/11 and 6-126/11 showed significantly larger shear strengths, compared with an untreated PSA with an even much higher gel content (i.e., PSA 5). This suggests that the discrete microgels in PSAs 4 and 6 transformed into continuous gel networks after post-treatment. In addition, the higher tack and peel strength of the PSAs 4-126/11 and 6-126/11 should



also be due to their smoother surfaces, compared with PSAs 4 and 6.

From Table VIII, one can see that after heating under the same conditions, PSA 4 showed a larger increase in gel content (i.e.,  $\sim 19$  wt %), compared with PSA 6 (i.e.,  $\sim 14$  wt %). This was because PSA 6 had a significantly larger amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ), compared with PSA 4. Some of these very small sol polymers (i.e.,  $M_x < M_e$ ) could not entangle with other polymer chains even at one end. Hence, during the heating process, they could not react with other polymers and become gel. Table VIII also showed that PSA 4-126/11 showed significantly larger shear strength than PSA 6-126/11 (i.e., 11.30 vs. 5.10 h). As the gel content differences between these two treated PSAs was small (i.e., 7 wt %), the significantly larger shear strength of PSA 4-126/11 should correspond to a more perfect continuous gel network compared with PSA 6-126/11. The formation of a less perfect continuous gel network in PSA 6-126/11 could be explained as follows: The presence of a significantly larger amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ) in PSA 6 should have caused much less entanglement between the sol polymers and the microgels, compared with PSA 4. Accordingly, the gel network of PSA 6-126/11 had more weak points around the edges of the original microgels compared with PSA 4. Moreover, PSA 4-126/11 exhibited significantly smaller tack compared with PSA 6-126/11 (i.e., 323 versus 450/m). It is suspected that the larger gel content of PSA 4-126/11 only played a minor role in achieving its much smaller tack, as the gel content differences between PSAs 4-126/11 and 6-126/11 were very small (i.e.,  $\sim 7$  wt %). The much smaller tack of PSA 4-126/11 compared with PSA 6-126/11 was likely due to its significantly higher surface roughness. This was because there were equal amounts of sol and gel polymer in PSAs 4 and 6 (i.e., gel content:  $\sim 50$  wt %). Considering the much larger mobility of the sol polymers compared with the microgel, the movement of sol polymers occurring during the heating process should have been the principal cause of the surface changes of the PSA films. PSA 6 had a significantly larger amount of very small sol polymers and these small sol polymers likely displayed greater mobility than the larger ones due to their much smaller size. Hence, the sol polymer in PSA 6 should have flowed much more during the heating process, compared with PSA 4. Consequently, PSA 4-126/11 should have higher surface roughness compared with that of PSA 6-126/11. The peel strength of PSA 4-126/11 was only slightly smaller than that of PSA 6-126/11 (i.e., 236 vs. 270 N/m). The much smaller difference in peel strength observed with PSAs 4-126/11 and 6-126/11 compared with the differences in tack, was because peel

strength is not as sensitive to surface smoothness of the PSA films as tack. During peel strength testing, a much longer contact time and also a much larger contact force were used compared to tack testing.

From the above results, one can see that increasing the amount of very small sol polymers in the original gel-containing latex-based PSAs had a significant negative influence on the performance of the treated PSAs. Decreasing the amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ) in the original gel-containing latex-based PSAs could lead to significantly better performance for the treated PSAs. For example, shear strength could be greatly increased only at a small sacrifice to peel strength.

#### **Influence of the amount of very large sol polymer in gel-containing latex-based PSAs on the performance of their treated PSAs**

Tobing et al.<sup>1</sup> found that after post-treating a gel-containing latex-based PSA with  $M_w$  (604 kg/mol) of about  $30M_e$  ( $M_e$ :  $\sim 20$  kg/mol), the PSA's performance could not be greatly improved. They pointed out that if the  $M_w$  of a gel-containing latex-based PSA is too large (e.g.,  $M_w > 20M_e$ ), then the microgel could not be turned into a continuous gel network after post-treatment. Since  $M_w$  is only an average number, we decided to study if increasing the amount of very large sol polymer (e.g.,  $M_x > 20M_e$ ) in a latex-based PSA under the conditions of  $M_c > M_e$  and also  $2M_e < M_w \leq 20M_e$  will have a significant influence on the performance of post-treated PSAs. For this purpose, PSAs 4 and 5 as well as their heated counterparts were studied. Their polymer microstructure and performance are shown in Table IX.

PSAs 4 and 5 both had  $M_c > M_e$  as well as  $2M_e < M_w \leq 20M_e$ . As shown earlier, both PSAs could form a continuous gel network. PSA 4 had a lower gel content and a larger  $M_w$  compared with PSA 5 (see Table IX). In addition, PSA 4 had a much larger amount of very large sol polymers (i.e.,  $M_x > 20M_e$ ), compared with PSA 5 (i.e.,  $\sim 30$  vs. 12 wt % of the total sol polymers). From Table IX, one can see that at a similar gel content of  $\sim 80$  wt %, PSA 4-126/21 showed a much smaller shear strength as well as similar tack and peel strength compared with PSA 5-126/11. It seems that tack and peel strength were mainly affected by gel content. Although the  $M_c$  of PSA 4-126/21 was not measured, based on the significantly smaller shear strength of PSA 4-126/21 compared with PSA 5-126/11, one can assume that a much less perfect continuous gel network formed in PSA 4-126/21.

This can be explained by examination of the film formation processes for latex-based PSAs and their heated counterparts. As shown in Figure 8, during

**TABLE IX**  
**Polymer Properties and Performance of PSA 4, 5 and Their Heated PSAs**

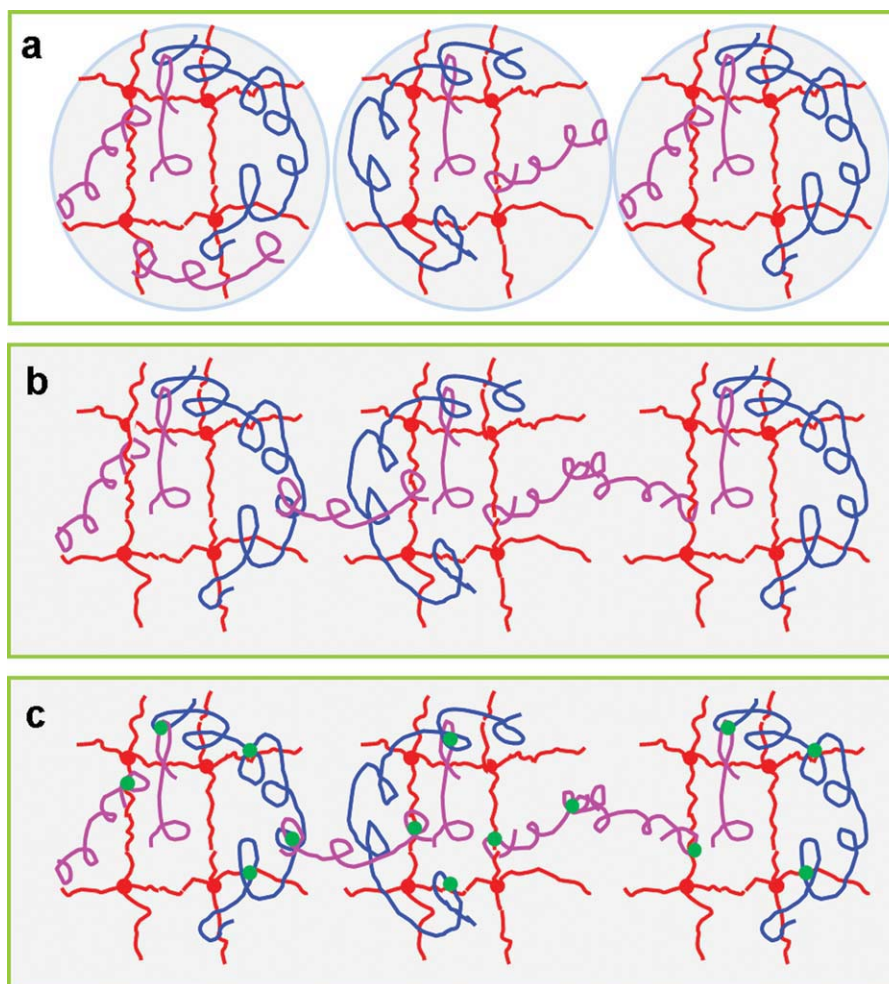
PSA ID	Gel content (wt %)	$M_w$	$M_n$	$M_c$	$M_e$	$x^{*a}$
		( $\times 10^3$ kg/mol)			(wt %)	
4	51	443	105	82	21	30
4-126/21	79	190	72	–	–	–
5	75	217	70	59	21	12
5-126/11	81	161	78	53	–	–
PSA ID	Tack (N/m)	Peel strength (N/m)		Shear strength (h, 1/2" $\times$ 1/2")		
4	216	185		0.52		
4-126/21	299	210		20.20		
5	176	104		1.10		
5-126/11	280	190		>336 h (two weeks) <sup>b</sup>		

<sup>a</sup>  $x^*$  refers to the weight percentage of the sol polymers with  $M_x > 20M_e$  in the total sol polymers. This number was obtained via GPC.

<sup>b</sup> No sign of shear failure of the PSA film was observed for more than 2 weeks.

the film formation process, some sol polymer chains of one latex particle could diffuse across particle boundaries. If their size was larger than  $2M_e$ , they

would be able to entangle two adjacent microgels. Due to their much larger size, the very large sol polymers (e.g.,  $M_x > 20M_e$ ) are not particularly



**Figure 8** Scheme of formation of original and post-treated PSA films from latex 4, which contains a significant amount of very large polymer chains (i.e.,  $M_x > 20M_e$ ) (a: Latex, b: Latex-based PSA film; and c: Post-treated PSA film 4-126/21; Note: The grid refers to a gel network; the dots refer to cross-linking points; the very long curly lines refer to very large sol polymer chains (i.e.,  $M_x > 20M_e$ ); and the other lines refer to medium size sol polymer chains (i.e.,  $2M_e < M_x < 20M_e$ ). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

TABLE X  
Polymer Properties and Performance of PSA 4, TK1, and Their Heated PSAs

PSA ID	Gel content (wt %)	$M_w$	$M_n$	$M_c$	$M_e$	$x^{*a}$
		$(\times 10^3 \text{ kg/mol})$			$(\text{wt } \%)$	
4	51	443	105	82	21	30
4-126/21	79	190	72	–	–	–
TK1 <sup>b</sup>	45	188	36	143	25	–
TK1-121/10 <sup>c</sup>	77	100	30	76	23	–
PSA ID	Tack (N/m)	Peel strength (N/m)		Shear strength (h, 1/2" × 1/2")		
4	216	185		0.52		
4-126/21	299	210		20.20		
TK1 <sup>b</sup>	193	246		0.83		
TK1-121/10 <sup>c</sup>	211	123		18.33		

<sup>a</sup>  $x^*$  refers to the weight percentage of the sol polymers with  $M_x > 20M_e$  in the total sol polymers.

<sup>b</sup> TK1 is a latex-based BA/AA/IBMA (isobutoxy methyl acrylamide) (weight ratio: 96.4/2.5/1) PSA (see Table IV of Ref. 1).

<sup>c</sup> TK1-121/10 is the PSA obtained by heating PSA TK1 at 121°C for 10 min (see Table IV of Ref. 1).

mobile, hence they tend to stay in their local latex particles and entangle with either the sol or microgel polymers there. In addition, due to their larger size and resulting densely entanglement with other small or medium size sol polymers in its local latex particle, these very large sol polymers might also slow the diffusion of other sol polymers during the film formation process as well as the conditioning process afterward. As a result, if there were a larger number of much larger sol polymers in the lattices, then the number of entanglement points for connecting two adjacent microgels would be much smaller in the corresponding latex-based PSAs. Consequently, fewer cross-linking points for connecting two adjacent microgels were formed in the heated PSAs, resulting in much lower shear strengths. In this case, a large portion of the gel increase caused by post-treatment was due to the reaction between the very large sol polymers with their nearby microgel and sol polymers. This kind of reaction cannot lead to the formation of a continuous gel structure as discussed earlier.

To confirm the above explanation with respect to the negative effect of very large sol polymer on the performance of heated PSAs, the heating of PSAs TK1 and 4 was studied. The polymer properties and performance of these two PSAs as well as their heated counterparts are shown in Table X. PSA TK1 is a latex-based PSA from a previous study reported by Tobing et al.<sup>11</sup> It has a film thickness of about 30  $\mu\text{m}$ , which is very close to the film thickness used in this study ( $\sim 33 \mu\text{m}$ ). In addition, its composition (i.e., BA/AA/IBMA (isobutoxy methyl acrylamide)/DDM (*n*-dodecyl mercaptan) weight ratio: 96.4/2.5/1/0.1) was homogenous and very similar to that of PSA 4 (i.e., BA/AA/HEMA weight ratio: 96/2/2).

Hence, the copolymers of these two PSAs should also have very similar  $T_g$ s. Tobing et al. showed the heating of PSA TK1 as a good example of transforming the microgels into a continuous gel network. Its heated counterparts, PSA TK1-121/10, showed significantly larger shear strength, compared with similar gel content unheated latex-based PSAs with the same composition. From Table X, one can see that PSA TK1 had a similar gel content but smaller  $M_w$  than PSA 4, hence it can be concluded that there was a much smaller amount of very large sol polymer in PSA TK1. The latex used for producing PSA TK1 should also have had a much smaller amount of very large sol polymers, compared with the latex used for casting PSA 4. Hence the sol polymers' diffusion rate during the process of forming and conditioning PSA TK1 should be much larger compared with that for PSA 4. If our previous explanation regarding the negative influence of very large sol polymers is correct, then using a shorter conditioning time for PSA TK1, compared with PSA 4, could lead to a similar amount of diffused sol polymers. Consequently, in this case, the microgels were entangled with similar amounts of sol polymers in both PSAs. Accordingly, their heated counterparts might have continuous gel networks with a similar degree of perfection, resulting in similar shear strength if the heated PSAs had similar gel contents. This was confirmed with the following experiment results. Tobing et al. made the heated PSA TK1-121/10 by directly drying the still wet PSA TK1 at a high temperature (i.e., 121°C for 10 min). Thus, the total time allowed for sol polymer diffusion in PSA TK1 was a maximum of 10 min before heating<sup>1,11</sup>; in contrast, in our study, before heating PSA 4, it was dried and conditioned at room temperature for 24 h.



**TABLE XI**  
**Polymer Properties of PSAs 5, TK2 and Their Heated Counterparts**

PSA ID	Gel content (wt %)	$M_w$	$M_n$	$M_c$	$M_e$
		( $\times 10^{-3}$ g/mol)			
5	75	217	70	59	21
5-126/11	81	161	78	53	-
TK2 <sup>a</sup>	0	271	75	-	23
TK2-121/10 <sup>b</sup>	80	79	30	63	23

<sup>a</sup> TK2 is a BA/AA (weight ratio: 97.5/2.5) statistical copolymer produced by solution polymerization (see Table I of Ref. 18).

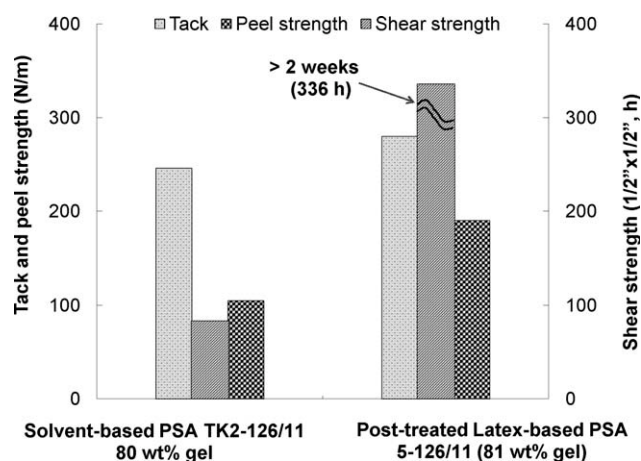
<sup>b</sup> TK2-121/10 is the PSA generated by heating the PSA film cast from the "TK2" copolymer solution at 121°C for 10 min (see Table IV of Ref. 18).

From Table IX, one can see that at similar gel contents (i.e.,  $\sim 78$  wt %), PSA TK1-121/10 showed similar shear strength ( $\sim 18.33$  h) as that of PSA 4-126/21 ( $\sim 20.20$  h). Based on this similar shear strength, one can conclude that similar gel content PSAs TK1-121/11 and 4-126/21 should have continuous gel networks with similar degrees of perfection.

#### Comparison of the performance of post-treated latex-based PSAs and solvent-based PSAs with similar microstructure

To check whether the performance of post-treated latex-based PSA can be improved to the same level as that of a solvent-based PSA with similar polymer microstructure, PSA 5-126/11 obtained from this study was compared with PSA TK2-121/10, a solvent-based PSA. These two PSA films had similar thicknesses of  $\sim 30$   $\mu\text{m}$ . In addition, as mentioned earlier and as shown in Table XI, PSA 5-126/11 was obtained by heating a high gel content latex-based PSA 5 (i.e.,  $\sim 75$  wt %). PSA TK2-121/10 was obtained from a gel-free PSA copolymer. PSA 5-126/11 and TK2-121/10 had a very similar copolymer composition: BA/AA/HEMA weight ratio of 96/2/2 for the former and BA/AA weight ratio of 97.5/2.5 for the latter. In addition, these two PSAs had very similar polymer microstructures (see Table XI for gel content,  $M_c$  and  $M_w$ ). Figure 9 shows that the post-treated latex-based PSA 5-126/11 yielded a better performance than the solvent-based PSA TK2-121/10. This was initially surprising, but can be explained. The higher tack and peel strength of PSA 5-126/11 might be caused by its smoother surface compared to PSA TK2-121/10. The much larger shear strength could be caused by two factors related to polymer microstructure: (1) the tighter gel network of PSA 5-126/11 compared with that of PSA TK2-121/10 (i.e.,  $M_c$ : 53 vs. 63 kg/mol). However, considering the small difference in  $M_c$ , this factor should not

have contributed a very large portion to the very large difference in shear strength; (2) The more perfect network of PSA 5-126/11 compared with that of PSA TK2-121/10. In our opinion, making the solvent-based PSA TK2-121/10 by heating a gel-free PSA film made with a polymer solution is like making post-treated latex-based PSAs by heating a gel-free latex-based PSA. The reason is the latter process did not involve microgels either, like the former one. As shown earlier, even for gel-free or very low gel content latex-based PSAs with  $M_w > 2M_e$ , the amount of very small sol polymers in the PSA had a significant negative influence on the degree of perfection of the gel network in the heated latex-based PSA. Accordingly, shear strength was greatly decreased. Based on this, it is suspected that in the original PSA (i.e., TK2) for making the solvent-based PSA (i.e., TK2-121/10), there might also have been a significant amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ) leading to a less perfect gel network for PSA TK2-121/10, compared to the post-treated latex-based PSA 5-126/11. In addition, the significant shear strength difference between PSA 5-126/11 and TK2-121/10 might be also related to their respective heating processes. From Table XI, one can see that the reaction rate between polymer chains during the heating process for forming PSA TK2-121/10 was much larger than that for forming PSA 5-126/11. For example, the gel content increased by 80 wt % within 10 min during the former process; while only 6 wt % within 11 min during the latter process. The very large gel content increase during the heating process for forming PSA TK2-121/10 means that the polymer chains reacted and thereafter incorporated into the gel network very quickly. Hence, the flow of these polymer chains during the heating process might have been very limited. This is different from what was reported earlier regarding the significant polymer flow during the heating process for forming



**Figure 9** Performance of solvent-based PSA TK2-126/11 and post-treated latex-based PSA 5-126/11.

PSA 5-126/11. As a result, in PSA TK2-121/10 there might still be some defects from its corresponding original PSA film TK-2. The gel network of PSA TK2-121/10 was discontinuous around these defects, and consequently this might have led to smaller shear strengths compared with PSA 5-126/11.

## CONCLUSIONS

Post-treatment by heating is a very effective way for improving the performance of latex-based PSAs, and the effect of treatment depends strongly on the polymer microstructures of the untreated latex-based PSAs. For gel-free or very low gel content latex-based PSAs, decreasing the amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ) under the condition that  $M_w > 2M_e$ , could lead to improved entanglement between the polymer chains. Consequently, this would lead to the formation of a more perfect continuous gel network in the post-treated PSA. As a result, the post-treated PSA would exhibit significantly larger shear strengths. As for gel-containing latex-based PSAs, if  $M_c$  is larger than or close to  $M_e$  and also the  $M_w > 2M_e$  and smaller or close to  $20M_e$ , the microgels could be connected by the sol polymers. Improving the connection between the microgels in the latex-based PSAs is the key to achieving better PSA performance (i.e., larger shear strength). As in our case, a more perfect continuous gel network would form in the treated PSAs. As noted earlier, a perfect gel network is a continuous one with evenly distributed cross-linking points and therefore with less weak points in its structure. Better connection between the microgels in the untreated latex-based PSAs could be achieved in three ways: (1) simultaneously and properly increasing the  $M_c$  and  $M_w$  for similar gel content PSAs; (2) decreasing the amount of very small sol polymers (i.e.,  $M_x < 2M_e$ ). The negative effect of very small sol polymers was due to its incapability to effectively entangle with the microgels as well as other sol polymers in the latex-based PSAs; and (3) decreasing the amount of very large sol polymers (i.e.,  $M_x > 20M_e$ ). The negative effect of very large sol polymer was caused by its lower mobility.

Compared with the latex-based PSAs with similar polymer properties, the treated PSAs showed much better performance. They exhibited not only significantly larger shear strengths but also much larger tack and peel strengths. The larger shear strength resulted because the gel network was continuous in the treated PSAs, while discrete in the untreated PSAs. The larger tack and peel strength was due to the much smoother surface of the treated PSAs. During the post-treatment process, the PSA polymer could flow and resulted in a much smoother surface for the treated PSAs compared with those of the untreated ones. In this study, it was also found that by optimizing the polymer microstructures of the latex-based PSAs, it was possible to generate a treated latex-based PSA with even better performance than that of a solvent-based PSA with similar polymer properties.

The authors thank the Natural Science and Engineering Research Council (NSERC) of Canada and Omnova Solutions for financial support. Dr. Gabriela Fonseca is gratefully acknowledged for assistance with the AFM measurements.

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