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The Effect of Polymer Microstructure and Thermal Post-Treatment on Latex-Based Pressure Sensitive Adhesive Performance

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Summary: Butyl acrylate/acrylic acid/2-hydroxyl methacrylate (BA/AA/HEMA, weight ratio: 96/2/2) latexes were produced via starved seeded semi-batch emulsion polymerization. The microstructure of the latex polymers was controlled by varying the amount of chain transfer agent (1-dodecanethiol). The latexes were characterized for gel content, M_c (molecular weight between two adjacent cross-linking points), M_w (molecular weight of sol polymers) and M_e (molecular weight between entanglements). From these latexes, PSA films were cast, dried, conditioned and then thermally post-treated at 120 °C to react the carboxyl and hydroxyl groups from the AA and HEMA units. Tack, peel strength and shear strength of the PSA films were then measured. The thermal post-treatment was shown to be an effective way to improve latex-based PSA performance. The effectiveness of the post-treatment was observed to depend on the polymer microstructure (M_c relative to M_e relative to M_w) of the untreated latex-based PSAs and on the gel content.

Keywords: adhesive; emulsion polymerization; microstructure; post-treatment; pressure-sensitive adhesive

Introduction

An important class of viscoelastic materials is known as pressure sensitive adhesives (PSAs). They are noted for their ability to adhere to a substrate upon the exertion of a very small force. PSAs are characterized for their adhesive performance using tack, peel strength and shear strength. Tack measures the strength of the PSA's bond to a substrate under short contact time and small contact forces. The peel strength of the PSA is measured as the force required to peel the PSA from a substrate. The cohesive strength, or shear strength, of the PSA relates to its capability to resist deformation under shear forces.

When attempting to manipulate PSA performance properties, one encounters a problem. Attempts to increase the PSA's shear strength (e.g., by adding cross-linking agents) result in lowering the PSA's ability to deform and flow. This reduces the PSA's ability to wet and adhere to the substrate. In other words, increases in shear strength often result in reductions in tack and peel strength.

Many PSA's are produced using solution polymerization techniques. Interest in more sustainable polymerization techniques has led to the development of latex-based (i.e., emulsion polymerization) PSAs. In terms of adhesive performance, solvent-based PSAs tend to exhibit much larger shear strength at similar tack and peel strength levels compared to latex-based PSAs. This is related to the nature of the gel network found in solvent-based PSAs compared to that in latex-based PSAs.[1] Solvent-based PSAs generally possess a continuous gel structure while latex-based PSAs tend to possess a discontinuous structure.

Some attempts to improve the performance of latex-based PSAs have included

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the use of functional groups, either as part of the latex or in a water-soluble cross-linker, to transform a discrete gel microstructure into a continuous one. In some cases, post-treatment of the PSA films (i.e., exposing PSA films to an elevated temperature) to react the functional groups was used. Most of these efforts were focused on functional group optimization to simplify the post-treatment process.[2–5] Of course, adhesive performance is also related to the polymer microstructure of the original latex.

Tobing et al.[1,6] related M_w (weight-average molecular weight of sol polymer) and M_c (molecular weight between two adjacent cross-link points) of the latex to the performance of post-treated PSAs. They established that for gel-free latex-based PSAs, if $M_w > 2M_e$, then a continuous gel network could form after post-treatment of the PSA (Note: M_e is the molecular weight between two adjacent entanglement points). On the other hand, for gel-containing PSAs, if $2M_e < M_w < 20M_e$ and $M_c > M_e$, then the discrete microgels could become a continuous gel network by post-treatment. Using the above conditions, significant increases in shear strengths were possible using post-treatment of the PSAs.

This paper summarizes our efforts to improve latex-based PSA performance by a post-treatment (i.e., heating) of the PSA films. This was accomplished by manipulating chain transfer agent concentration to generate a series of latexes that meet the criteria proposed by Tobing and Klein. These PSA films were then heated to identify which would lead to better PSA performance.

Experimental Part

Materials

Butyl acrylate (BA), acrylic acid (AA), and 2-hydroxyl methacrylate (HEMA) monomers, 1-dodecanethiol (NDM) chain transfer agent (CTA), sodium dodecyl sulphate (SDS) surfactant, sodium bicarbonate ($NaHCO_3$) buffer, potassium persulfate (KPS) initiator and hydroquinone (HQ) inhibitor were 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_2O for pH control) was obtained from British Drug House. All solvents used in the polymer characterization were also used as supplied by the manufacturer. Nitrogen gas (Linde Canada) was used to purge the reactor. PTFE porous membranes with pore size of 0.2 μm, for use in gel content measurements, were purchased from Cole-Parmer Canada.

Latex Preparation

BA/AA/HEMA (weight ratio: 96/2/2) latexes were produced via a starved seeded semi-batch emulsion polymerization. The polymerization process included a brief batch stage to make seed latexes, a long feeding stage to further grow the latex particles, and a short cook stage to ensure the complete reaction of any residual monomer. The initial charge, except for the initiator solution and monomers, was added to a one-litre Mettler-Toledo LabMax™ reactor at room temperature. Stirring speed was maintained at 250 rpm. 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 1) 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 for the cook stage. The latex was then cooled to below 30 °C. After polymerization, hydroquinone was added to the latex to stop the reaction. Ammonia and DDI-water were added to

Table 1.
Polymerization formulations.

Ingredients	Initial charge (g)	Semi-batch Feed (g)	
		Monomer emulsion	Initiator solution
H_2O	202/15*	89	90
KPS	0.4	–	0.90
BA	11.58	324.48	–
AA	–	6.76	–
HEMA	–	6.76	–
NDM (CTA)	–	0–0.4 phm**	–
SDS	0.45	4.25	–
$NaHCO_3$	0.05	–	–

*Water used for initiator solution in seed production stage. **phm = parts per hundred parts monomer.

Table 2.
Latex properties.

Latex ID	CTA (phm)	Gel content (wt%)	M_w	M_c	M_e
			(x10^{-3} g/mol)		
1	0.20	0	252	N/A	26
2	0.15	13	470	N/A	22
3	0.10	36	656	N/A	22
4	0	75	217	59	21

adjust the pH to ~5.5 and a solids content of ~45 wt%. The microstructure of the latex polymers was controlled by varying the amount of CTA during the feeding stage of the polymerization process (see Table 2).

PSA Film Preparation

Details on the preparation and post-treatment of PSA films are given elsewhere[7–10] but are summarized here. Latexes were coated on a Mylar sheet with a #30 Meyer rod to yield PSA films with thicknesses of ~33 μm. The films were dried and conditioned (24 h at 23 °C and relative humidity of 50%) prior to testing. Post-treatment involved a two-step procedure beginning with heating at 90 °C for 10 min to remove residual water in the PSAs followed by heating at a higher temperature (e.g., 120 or 126 °C) to react the carboxyl and hydroxyl groups from AA and HEMA units. The post-treated PSA films were conditioned (24 h at 23 °C and relative humidity of 50%) prior to testing.

Characterization

Detailed testing procedures for gel content, M_c, M_w and M_e measurement were described previously.[7–10] The swelling method[1] 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.[11] 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.[12] Details of the testing procedures were also provided previously.[7–10]

Results

A schematic representation of various polymer microstructures is shown in Figure 1. [10] Figure 1-a depicts the continuous gel structure of a solvent-based PSA film. One observes the gel polymer with cross-link points as well as the presence of sol polymers of various lengths. The longer sol polymer chains, those with chain lengths $>2M_e$, are capable of entanglement, while the smaller ones are not. Figure 1b depicts the distinct particles of a latex-based PSA film during the film casting process. The water in the latex will evaporate and one would expect that some sol polymers will diffuse across the particle boundary into an adjacent particle. If the latex polymer microstructure satisfies Tobing and Klein's condition (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.[1,6] As the drying process continues, the latex particles deform, particle boundaries gradually disappear, and the PSA film forms (Figure 1c). Comparing Figure 1c to 1a, one observes that the gel is discrete in the latex-based PSA film and the small microgel polymers are connected strictly by sol polymer chain entanglement. This would represent an ideal case as one would expect that the microgels may not necessarily entangle. This discrete gel structure is often the cause for the lower

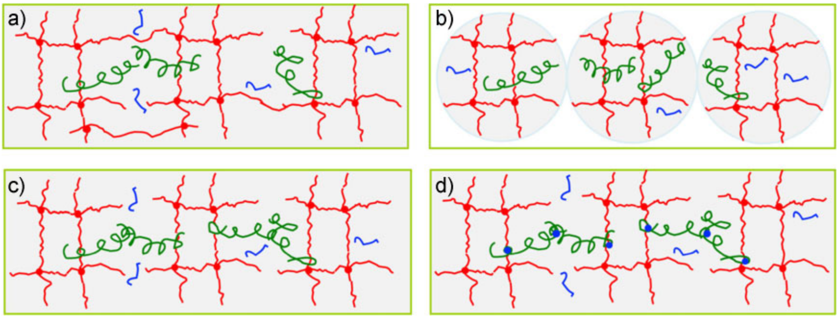

Figure 1.
Schematic representation of the polymer microstructures of PSA films and latexes, as well as the latex-based PSA film formation process. (a: solvent-based PSA film, b: latex particles, c: latex-based PSA film, d: post-treated latex-based PSA film.) (Note: In images a through d, the grids and associated solid dots represent the gel polymers and their cross-link points, respectively. The long curled lines represent sol polymers with chain length $> 2M_e$; 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).[10]

shear strength exhibited by latex-based PSA films compared to that of their solvent-based counterparts. Finally, in Figure 1-d, we propose that if the latex-based PSA polymer contains certain functional groups, a post-treatment (i.e., temperature elevation) of the PSA film will result in the transformation of some entanglement points into cross-linking points. The discrete gel structure would then become a more continuous one and we would expect the shear strength to increase.

Of further concern would be the uniformity of the continuous gel structure formed as a result of a post-treatment (Figure 1-d). The presence of weak or non-crosslinked areas in the microstructure could lead to a reduction in cohesive strength and thus, inadequate shear strength. To overcome these weaknesses, the polymer microstructure of the untreated PSA film should be well entangled. This can be achieved by manipulating the chain transfer agent and cross-linker concentrations in the latex formulations.

Four separate latexes were produced according to the formulation in Table 1. A range of latexes with differing gel contents were produced by manipulating the CTA concentration (Table 2). Despite the absence of cross-linker, gel was still produced and these latexes would be capable of forming a continuous network if the AA and HEMA are reacted after heating the PSA film. We note the increase in molecular weight of the sol polymer, M_w, with decreasing CTA concentration, as expected. One exception to the trend is latex 4 where significant gel is produced. This occurred because the gel was produced from the larger sol polymers and what remained were the lower molecular weight sol polymers.[13]

The adhesive performance of the PSA films cast from latexes 1–4 is shown in Figure 2. During adhesive testing, gel-free

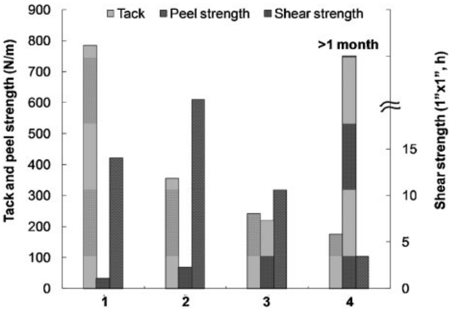

Figure 2.
Performance of PSAs from latexes produced without cross-linker (latexes 1–4). (Shear strength measures were on a 1"x1" area of a stainless steel panel).

latex 1 showed cohesive failure while all other latexes showed adhesive failure. One observes the expected trends in tack, peel strength and shear strength. With the increase in M_w, tack tended to decrease, while peel strength first increased and then decreased. In contrast, the shear strength increased with gel content. It should be noted that the values for shear strength of these PSA films were not particularly high. This is consistent with the criteria that would ensure entanglement of the sol polymers with the microgel (i.e., $M_w > 2M_e$ and $M_c \geq M_e$). The M_e for latexes 1–4 was in the range of 20,000 and thus, all four latexes had $M_w > 2M_e$ but all but latex 4 possessed enough gel to yield $M_c \geq M_e$. Thus, the PSA cast from latex 4 possessed a shear strength well above that of the others (>1 month).

The poorly performing gel-free PSA films from latex 1 were then heated to generate crosslinking reactions between the carboxyl and hydroxyl groups from AA and HEMA units in the polymer. Three temperatures (i.e., 120, 126 and 131 °C) were used to heat the PSA at heating times of 10, 20 and 30 min. The gel content of the original and heated PSA films is shown in Figure 3 whereas the PSA performance is shown in Figure 4–6.

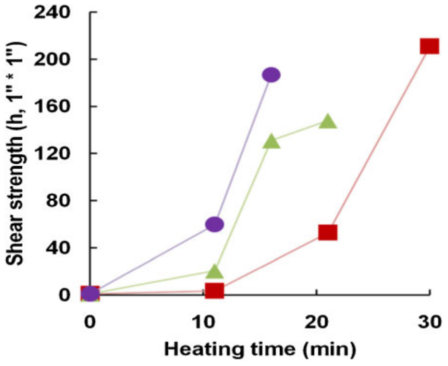

Figure 4.
Change in shear strength for post-treated PSA films from gel-free latex 1. (Symbols represent heating temperatures: 131 °C = circles; 126 °C = triangles; 120 °C = squares).

The gel content increased with both heating time (e.g., from 0 to 38 wt% at 120 °C) and temperature (Figure 3). We also observed an initial increase in M_w with gel content to a maximum at 15 wt% (for PSA at 120 °C) followed by its decrease in value. This trend in M_w was observed for all the PSAs shown in Table 2. The maximum in M_w is explained by the reaction between the carboxyl and hydroxyl groups from the AA and HEMA units to form larger polymer chains. A resulting chain of sufficient length would become gel polymer; otherwise, it would remain sol polymer. At insufficient heating times, most of the sol polymers grew into larger sol

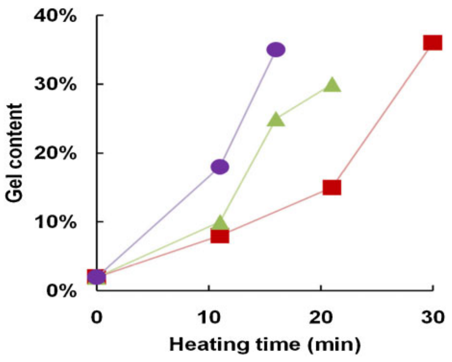

Figure 3.
Gel content change for post-treated PSA films from gel-free latex 1. (Symbols represent heating temperatures: 131 °C = circles; 126 °C = triangles; 120 °C = squares).

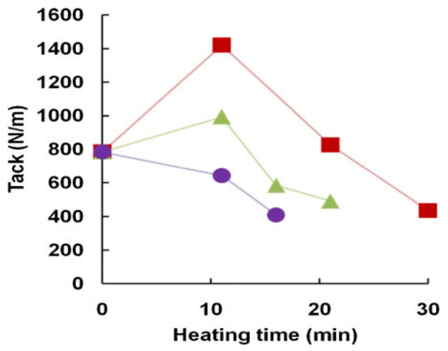

Figure 5.
Change in tack for post-treated PSA films from gel-free latex 1. (Symbols represent heating temperatures: 131 °C = circles; 126 °C = triangles; 120 °C = squares).

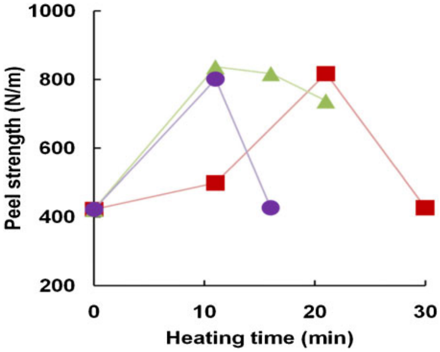

Figure 6.
Change in peel strength for post-treated PSA films from gel-free latex 1. (Symbols represent heating temperatures: 131 °C = circles; 126 °C = triangles; 120 °C = squares).

polymers with only a small fraction becoming gel polymers; hence, the increase in M_w with gel content. Additional heating resulted in more significant gel content. Because these gel polymers arose primarily from the larger sol polymers, the conversion of the larger sol polymers into gel polymers resulted in a decrease in the average size of the sol polymers (M_w). This assumes that the condensation reaction is consistent with our earlier explanation for molecular weight and gel content changes based on a free-radical kinetic mechanism.[13] In other words, we assume that chain diffusion is not playing a significant role when the polymer is in the solid film state.

The expected increase in shear strength with gel content (Figure 4) was observed, while tack (Figure 5) and peel strength (Figure 6) displayed maxima. This PSA performance trend is similar to that previously observed with unheated latex-based PSA films.[9] The increased gel content resulted in improved cohesive strength and thus, larger shear strength. At the same time, larger cohesive strength decreased the PSAs' deformability and flow ability, leading to less wetting of the PSA on the substrate during the bonding process. In addition, the higher gel content lowered the PSA's capability for elongation[7] and consequently, the higher gel content PSAs could experience a much smaller strain during the debonding process.[14,15] In other words, PSAs with larger gel contents dissipated less energy during the debonding process. Less wetting and less energy dissipation led to a decrease in tack and peel strength with increasing gel content.

At very low gel contents (i.e. from 0 to 15 wt%) tack and peel strength increased with gel content. This was due, in part, to the negligible negative effect of gel on decreasing the PSAs' elongation capability and to the increase of M_w with gel content, as discussed earlier. 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.

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