

Effect of Particle Structure on the Peel Strength and Heat Resistance Properties of Vinyl Acetate/Acrylate Latexes Laminating Adhesives

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ABSTRACT: The concept of using particle structure design to prepare emulsion laminating adhesives (LAs) for improving both the peel strength and heat resistance properties has been investigated. The homogeneous particle latices based on vinyl acetate/acrylate copolymer (samples 1–3) were synthesized by seeded semicontinuous emulsion polymerization with different chain transfer agent (CTA) contents but with no functional monomers, while the core-shell structure crosslinkable latices (samples 4 and 5) were prepared through multistage polymerization technique. The emulsion particle structure was investigated by TEM and particle size analyzer. The results indicate that the average emulsion particle diameter is about 130 nm and the particles grow without secondary nucleation. Samples 1 and 2 prepared with 0.7 and 0.5 phm (per hundred gram monomer) CTA respectively, show high peel strength but

poor heat resistance property. On the contrary, the sample 3 prepared with 0.1-phm CTA exhibits low peel strength but relatively good heat resistance. However, sample 4, which was synthesized with 0.5-phm CTA and 0.4-phm acetoacetoxy ethyl methacrylate (AAEM) in core but 0.5-phm CTA and 0.6-phm AAEM in shell stages, shows high peel strength (1032.9 g/in.) and good heat resistance property (524.9 g/in.). In addition, sample 5 also demonstrates high peel strength (987.2 g/in.) and good heat resistance property (643.5 g/in.) when it was synthesized using 0.1-phm CTA but no AAEM in core, 0.36-phm CTA and 0.75-phm AAEM in shell stages. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2857–2865, 2011

Key words: core-shell emulsion; laminating adhesives; crosslinking; peel strength; heat resistance; particle design

INTRODUCTION

Today, more and more adhesives are used as laminating adhesives (LAs) to prepare flexible packaging by laminating various polymeric films to other films.^{1–4} LAs are available in a variety of technologies, viscosities and solid concentrations. In the past, the solvent based LAs were utilized mostly because of fast volatilization of organic solvent, low surface tension and continuous crosslinking network morphology. However, for their increasing costs, flammability, pollution considerations, as well as the government regulations for laminating converters to reduce volatile organic solvents from solvent based adhesives, many solvent based LAs were replaced by emulsion LAs, especially by acrylate copolymers latices. Despite the aggressive efforts to substitute solvent based LAs,^{5–7} there are still high performance packaging applications that can only be met by solvent based LAs. The majority of these applications require a high temperature resistance together with green tack. It is known

that solvent-based LAs have a much higher heat resistance than that of emulsion counterparts. This is due to the continuous crosslinking networks in the film by post curing technique.⁸ In contrast, acrylate copolymers LAs prepared by emulsion polymerization produce microgels that retain their discrete morphology in the film.^{9–12} Meanwhile, for the sake of well film formation performance, the emulsion adhesives are very soft, weak, and tack polymers. So a crosslinkable structure would be essential to the polymer chains of emulsion LAs and the perfect conditions for crosslinking reactions are crosslinkable under room temperature and during cure process. Consequently, the LAs are capable of postcrosslinking to obtain high adhesion performance similar to that of solvent based LAs. To introduce crosslinking structures to the emulsion is well studied in pressure sensitive adhesives (PSAs) and coatings.^{9–19} Recently, Mishra et al. synthesized LAs using glycidyl methacrylate (GMA), methyl methacrylate (MMA), and butyl acrylate (BA) as comonomers.²⁰ They reported that the polymer chains had epoxy groups and the adhesive properties could be improved by crosslinking reaction of functional groups after laminating. Also, they reported a PET/PE (12 μm and 20 μm , respectively) laminating film with 420 g/in. T-peel strength.

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TABLE I
Recipes of Pre-Emulsion for the Adhesives Samples

	Sample 1	Sample 2	Sample 3	Sample 4		Sample 5	
				Core	Shell	Core	Shell
VAc (g)	40.0	25.0	50.0	20.0	12.5	20.0	12.5
MMA (g)	0	15.0	0	3.5	7.5	3.5	7.5
BA (g)	60.0	60.0	50.0	26.5	30.0	26.5	30.0
AAEM (g)	0	0	0	0.4	0.6	0	0.75
AA (g)	0.8	0.8	0.8	0.4	0.4	0.4	0.4
Dm (g)	0.7	0.5	0.1	0.25	0.25	0.05	0.18
CO-436 (g)	0.5	0.5	0.5	0.25	0.25	0.25	0.25
ABS-23 (g)	2.5	2.5	2.5	1.25	1.25	1.25	1.25
Water (g)	50.0	50.0	50.0	25.0	25.0	25.0	25.0

However, they did not study the heat effect on the bonding strength of the LAs.

In this work, emulsion LAs with different particle structures were synthesized by seeded semicontinuous emulsion polymerization. Some of resulted latices copolymers contained acetoacetoxy groups which could react with the postadded crosslinking reagent (ADH). Then the polymeric films were bonded by the emulsion LAs to study the effects of particle structure, crosslinking and gel on the peel strength and heat resistance properties. In this research, to obtain the true T-peel strength tested at different temperature and avoid the tearing caused by tear sensitive films such as biaxial oriented polypropylene (BOPP), the two same 45- μm corona treated polyethylene (PE) films were laminated.

EXPERIMENTAL

Materials

Vinyl acetate (VAc), MMA, *n*-BA, and acrylic acid (AA) monomers were purchased from Kelong Chemical Reagent Factory (Chengdu, China). AAEM (Lonza) was used as a functional monomer. All the monomers were treated by sodium hydroxide aqueous solution (5 wt %) to remove inhibitor prior to polymerization. Adipic dihydrazide (ADH) was purchased from Best-Reagent (Chengdu, China) as a crosslinking agent. Ammonium sulfate polyoxyethylene nonyl phenol (CO-436) and sodium dodecyl benzene sulfonate solution (ABS-23) used as surfactants were kindly provided by Professional Chemical Product (Shanghai, China). *N*-dodecyl mercaptan (Dm) was used as chain transfer agent (CTA), ammonium persulfate (APS) as initiator and sodium bicarbonate (NaHCO_3) as buffer. Distilled water was used in all experiments. PE (45 μm , corona treated) films were used as laminated films.

Synthesis of emulsion laminating adhesives

The pre-emulsion was prepared by mixing (stirring rate 300 rpm) the aqueous and organic phase. The

aqueous phase was a mixture of fixed amounts of hydrophilic monomer (AA), surfactants, and water; the organic phase was a mixture of the hydrophobic monomers (VAc, MMA, BA, AAEM) and CTA (Dm) (Table I).

Copolymers latices (samples 1–3) were synthesized by pre-emulsification semicontinuous emulsion polymerization. The copolymerization reactions were carried out in a 500 mL four-neck glass reactor equipped with mechanical stirrer with stainless steel paddles (120 rpm), reflux condenser, thermometer and two dropping funnels. The reactor was fixed in a temperature controllable water bath, charged with 0.35 g buffer, 0.2 g AA, and 65 g water and thermostated at 80°C. After 5 min, 3.2 g 6.25 wt % initiator aqueous solution was added with a funnel and 5 min later 15.4 g pre-emulsion. After 20 min, a self-seeded emulsion was prepared. Then, 6.4 g of the initiator solution and 138.7 g of the pre-emulsion were dropped from the respective funnels during 4 h. Finally, the system was kept with stirring for 2 h (postpolymerization time) and cooled rapidly to 40°C. The pH was between 4 and 5.

The emulsion LAs of the samples 4 and 5 were synthesized by a “core-shell” multistage polymerization technique. The detailed polymerization procedure was similar to the above manner, but 15.4 g core pre-emulsion instead of 15.4 g pre-emulsion was added, 20 min later, the remaining core pre-emulsion was added, and the shell pre-emulsion was added subsequently.

The samples 4+A and 5+A were prepared through postadding crosslinking reagent ADH into the samples 4 and 5, respectively, (the molar ratio of ADH : AAEM = 1 : 2).

Characterization

Monomer conversion

The monomer conversion was calculated gravimetrically. The fractional weight conversion is defined as the fraction of monomer that had been polymerized.

FTIR analysis

The dry films of samples were characterized using a Magna-IR-560 FTIR (Nicolet/America) spectrometer with a resolution of 4 cm^{-1} .

T_g

T_g of dry adhesive samples was measured by a differential scanning calorimeter (DSC) (NETZSCH, Germany). DSC scans were recorded at the temperature ranging from -60 to 60°C at a heating and cooling rate of $10^\circ\text{C}/\text{min}$. In the first heating run, the samples were heated to 60°C , cooled to -60°C , and then heated from -60 to 60°C . The last run was analyzed. T_g was calculated from the peak of the first derivative of the inflection in the DSC curve.

Gel content

The gel content of samples was determined gravimetrically. A known amount of sample ($\sim 0.2\text{ g}$ of dried adhesive) sealed in filter paper (the mesh size is $1\text{--}3\ \mu\text{m}$) was put in a Soxhlet extraction with tetrahydrofuran (THF), under reflux for 24 h. After the extraction process, it was washed with fresh THF to remove any soluble polymer. Finally it was dried in a vacuum oven at 120°C for 1 h and weighted. The gel content was calculated using the following equation:

$$\text{Gel content (\%)} = W_g/W_p \times 100$$

where W_g is the weight of insoluble polymer (g) and W_p is the weight of dried polymer taken initially (g).

Molecular weight determination

The molecular weight (number average molecular weight (\overline{M}_n) and weight average molecular weight (\overline{M}_w) and molecular weight distribution of the soluble fraction of polymer were determined by using Waters size exclusion chromatography. The samples were dissolved in (1% w/v solution) THF, and THF was used as carrier solvent at a rate of $1\text{ mL}/\text{min}$. Narrow polystyrene standards having molecular weight range from 4×10^2 to 1×10^6 were used for calibration.

Morphological characterization

The morphology of emulsion particles was characterized using transmission electron microscopy (TEM; Hitachi, Japan). The emulsion samples diluted with aqueous solution (1.5 wt %) of phosphotungstic acid (negative staining) were placed on copper grids covered with formvar and dried under ambient temperature.

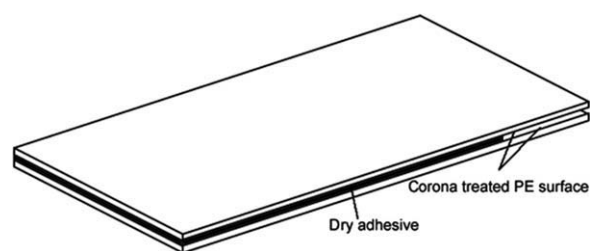


Figure 1 Sketch of laminate.

Particle size and distribution

The particle size and distribution were determined by laser light scattering particle analyzer (Mastersize 2000, Malvern, England). The area average particle diameter and volume average particle diameter are defined as follows:

$$\text{Area average particle diameter: } D_{[3,2]} = \frac{\sum ND^3}{\sum ND^2}$$

$$\text{Volume average particle diameter: } D_{[4,3]} = \frac{\sum ND^4}{\sum ND^3}$$

Peel strength test

Preparation of laminates. The laminate preparation for the adhesive performance testing was done in accordance with ASTM D1876.²¹ The laminating method was dry lamination. The emulsion adhesive was coated on one of the PE substrates with a bar coater and the coated film was passed through a drying oven (65°C) to remove water before the substrates were joined. The dry adhesive thickness was $\sim 10\ \mu\text{m}$. A second PE substrate was then combined with the first dry and coated film via a hot-nip rolling operation (65°C , 60 rpm). The resulting laminates were conditioned for 24 h at 55°C (making the adhesive flow uniformly or cure) before testing. The standard specimens (25-mm wide by 305-mm long) were cut from the laminates (Fig. 1).

T-peel strength under different temperature. According to ASTM D1876, the T-peel strength of the samples at different temperature (23, 40, 50, and 60°C) was determined by a tensile testing machine (YH-8812DH, Changping Ruihua, Dongguan, China) with a temperature controller. The sketch of T-peel strength test device was showed in Figure 2. Ten specimens were tested for each emulsion adhesive. The average T-peel strength was calculated and given in g/in.

RESULTS AND DISCUSSION

Monomer conversion and IR

The coagulation occurred during polymerization tends to reduce the solid content of latices and

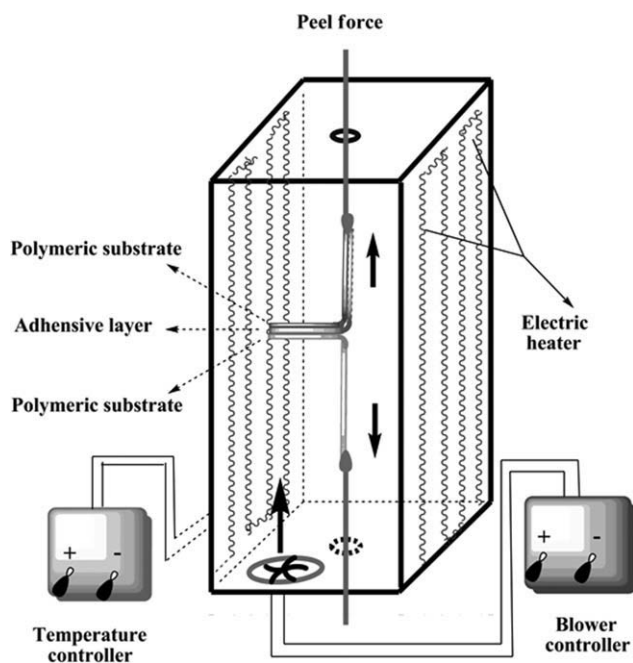


Figure 2 Sketch of T-peel strength test device.

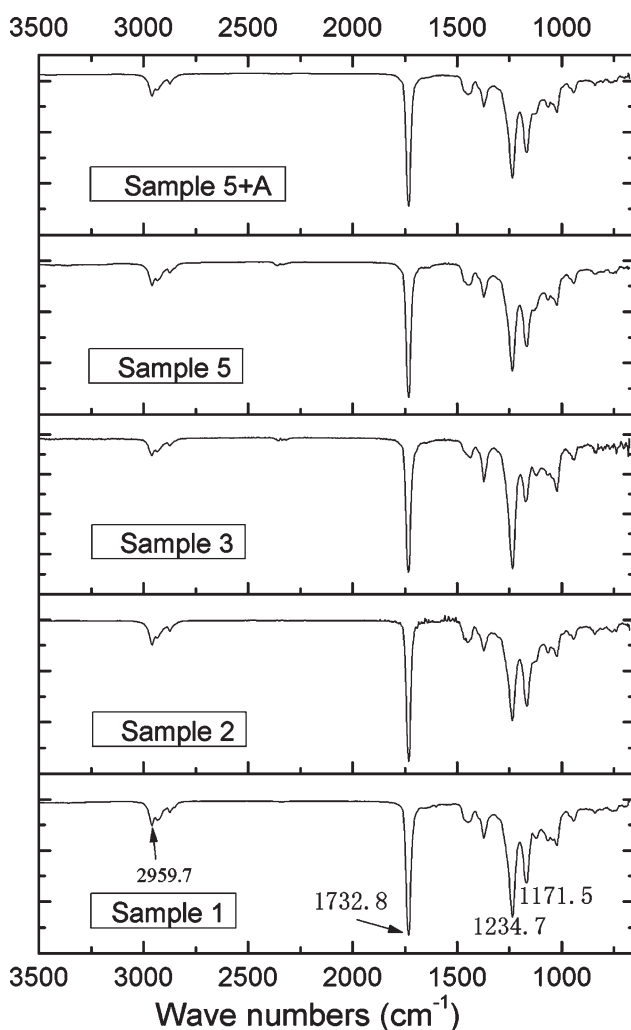


Figure 3 Infrared spectra of samples.

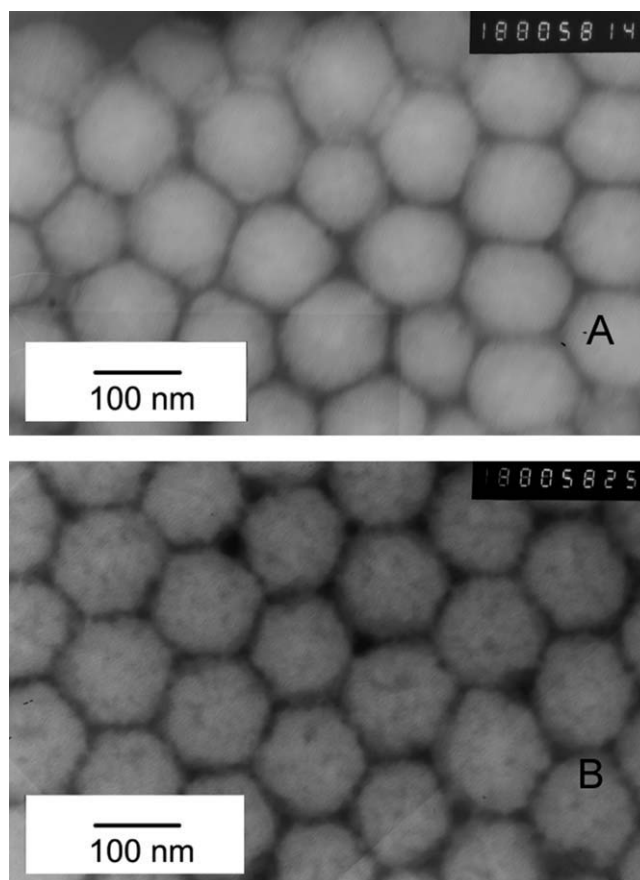


Figure 4 TEM images of sample 3 (A) and sample 5 (B).

compromises the latices stability. Generally, the coagulation is affected by surfactant content, solid content, AA content, polymerization temperature, stirring speed, initiator content, and polymerization technique.¹⁶ Therefore, the factors were optimized through a series of experiments to obtain very little coagulation (about 0.12 wt %) and stable latices for the following investigations. The recipes in this study were completed successfully with monomer conversions exceeding 99 wt %.

The infrared spectra of samples is shown in Figure 3. The bands at 2959.7 and 1732.8 cm^{-1} are due to $\nu(\text{CH}_3, \text{CH}_2)$ and $\nu(\text{C}=\text{O})$, respectively, the bands of 1234.7 and 1171.5 cm^{-1} are due to $\nu(\text{C}-\text{O}-\text{C})$ in the copolymer molecule. Because the similar recipes and low functional monomer contents (<1 wt %) were used, FTIR was not sensitive enough to

TABLE II
The Particle Diameter and Particle Size
Distribution of Samples 3 and 5

Sample	$D_{[3,2]}$ (nm)	$D_{[4,3]}$ (nm)	Particle size distribution ($D_{[4,3]}/D_{[3,2]}$)
3	109	148	1.417
5	104	139	1.406

TABLE III
Average Molecular Weight and Molecular Weight Distribution with Variable CTA Contents

Sample	1	2	3	4	5
CTA amounts (phm)	0.7	0.5	0.1	0.5 (core) + 0.5 (shell)	0.1 (core) + 0.36 (shell)
M_n (g/mol)	15013	18765	21193	16508	21243
M_w (g/mol)	41779	62070	73279	62014	88397
PDI	2.78	3.31	3.46	3.76	4.16
Peel strength ^a (g/in.)	1032.9	982.1	232.8	823.3	850.4

^a The peel strength was determined at 25°C.

distinguish resonance peaks from such small amounts of AA, AAEM, and ADH in this study.

TEM and particle size analysis

Figure 4(A,B) show the transmission electron micrographs of samples 3 and 5, respectively. For the similar recipes of samples and the same polymerization condition (such as the same emulsifier content) the samples 3 and 5 were expected to have similar particle morphology and the same particle size. As shown in Figure 4, the particle morphology and diameter of samples 3 were similar to that of the sample 5 with average diameter of 131.4 and 134.1 nm, respectively. However, it was hard to distinguish the shell from the core in the Figure 4(B) of sample 5 due to the similar vinyl acetate/acrylate copolymers of core and shell.

Table II shows that the samples 3 and 5 had similar diameters and the particle size distribution were 1.417 and 1.406, respectively. For the recipes of all the samples mentioned in this research, a small amount of hydrophilic monomer (AA) and the low monomer feeding speed limited the homogeneous nucleation in emulsion polymerization process. It is reasonable to infer that there was scarcely or no secondary nucleation in the emulsion polymerization process. With regard to sample 4 and 5, the core particles acted as seeds and the shell monomers were mainly polymerized on the core particles surface.

Average molecular weight and gel content

It has been known that the molecular weight and gel content are the significant factors affecting the performance of PSAs, wherein increasing molecular weight and gel content will increase the bonding strength of adhesives but decrease tack.¹⁶ These principles are applicable for LAs.

The molecular weight will affect LAs performance, especially the ability to wet the substrates. Therefore, the molecular weight of the THF-soluble polymer fractions was determined by GPC to interpret the relationship between peel strength and molecular weight. The results are listed in Table III. With the high CTA amounts (0.7 phm), sample 1 showed the

lowest \bar{M}_w , while with a low CTA content (0.1 phm) sample 3 showed the highest \bar{M}_w . As 0.5 phm CTA used, the sample 2 showed midrange \bar{M}_w between the samples 1 and 3. With regard to sample 4, with the same 0.5-phm CTA content used at core and shell stages, the \bar{M}_w and polydispersity index (PDI) were similar to that of sample 2. However, due to different CTA contents used (0.1 phm at core and 0.36 phm at shell) the sample 5 showed a high \bar{M}_w and a broad molecular weight distribution. Furthermore, on the high molecular weight range, samples 3 and sample 5 showed the higher \bar{M}_w , sample 4 demonstrated the low \bar{M}_w , which was similar to that of sample 2, but the sample 1 showed the lowest \bar{M}_w (Fig. 5). So it is reasonable to raise the idealized particles structure for samples 4 and 5. As shown in Figure 6, the core and shell of sample 4 were low \bar{M}_w copolymers containing crosslinkable acetoacetoxy groups from AAEM used during core and shell polymerization stages (0.4 phm in core and 0.6 phm in shell). The core of sample 5 was high \bar{M}_w copolymers with no crosslinkable groups, while the shell was low \bar{M}_w copolymers containing crosslinkable groups from AAEM (0.75 phm used in shell).

Gel fractions determined by removing water- and THF-soluble fractions are listed in Table IV. The gel amount is dependent on the amount of crosslinked polymer structures as well as on the amount of

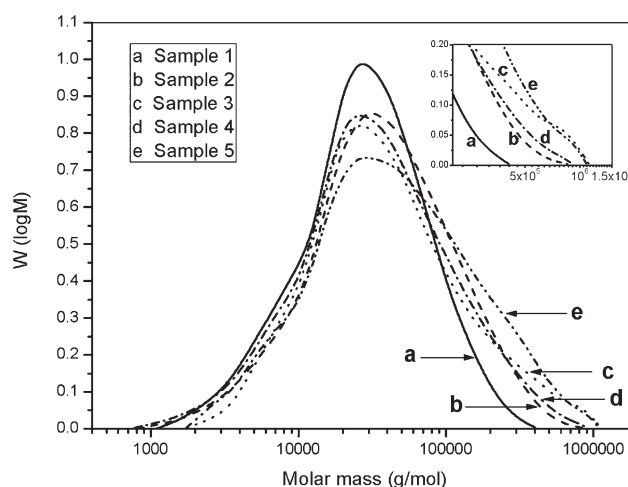


Figure 5 Molecular weight and distribution of samples.

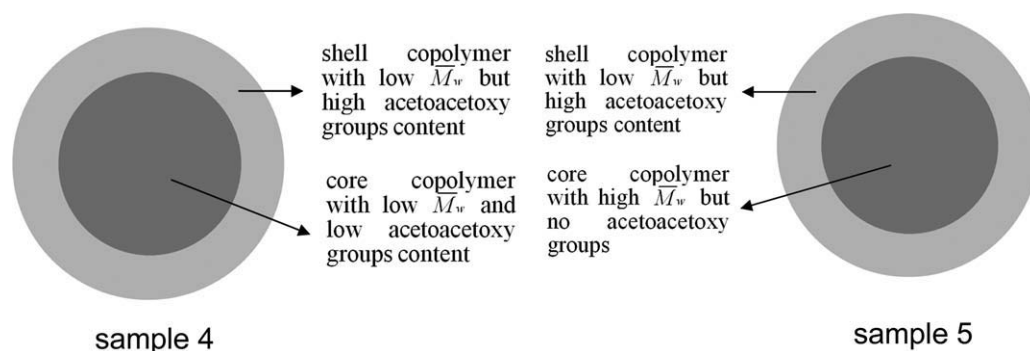


Figure 6 Schematic diagrams of idealized particle cross sections for designed emulsion particles of the samples 4 and 5.

entangled and coiled polymer chains. In latter case, the crosslinking network structure occurs through the entanglement between polymer chains. When molecular weight and branched chains increase, the gel amount increases. As CTA amount was 0.1 phm, sample 3 had a gel content of 55.97 wt %. However, as higher CTA contents (0.5, 0.7 phm) used, the samples 2 and 1 showed relatively low gel contents (5.02 and 5.55, wt %, respectively). For 0.5-phm CTA used both in core and shell process, the core-shell sample 4 showed a low gel content of 6.64 wt %. Because of 0.1-phm CTA used in core and 0.36-phm CTA in shell, the gel content of sample 5 was up to 60.5 wt %.

As shown in Table IV, the gel content of sample 4+A increased to 9.44 wt % and sample 5+A to 63.62 wt %, respectively. That was due to the presence of crosslinking structure resulted by the crosslinking reactions between the postadded ADH and the polymer chains among different particles or within the same particle.

Differential scanning calorimeter

T_g is another significant factor affecting the performance of lamination adhesives. Low T_g causes the adhesive to flow uniformly and wet the surface of substrates at the "cure" temperature to enable the formation of the adhesion bond (or initial tack). However, too low T_g could negatively impact the cohesive strength of the adhesive to resist heat. The T_g of samples was shown in Figure 7. According to the recipes, the T_g of the samples calculated using Fox equation²² was about -20°C . However, due to the

crosslinking, the T_g of all samples was higher than the calculated value (-20°C). For samples 1–3, the \bar{M}_w and the crosslinking degree (results of branched polymers) increased with CTA contents decreasing. Therefore the T_g increased with the CTA amount decreasing. Because of the crosslinking caused by the crosslinking reaction between copolymer and postadded ADH, the T_g of sample 4+A was higher than that of sample 2. Due to the crosslinking structure caused by the crosslinking reaction and higher molecular weight, the T_g of sample 5+A was higher than that of sample 4+A.

T-peel strength

The T-peel strength results of laminated films at different temperature are shown in Figure 8. At low temperature (25°C), the sample 3 showed a low T-peel strength (only 232.8 g/in.). While the samples 1 and 2 showed higher T-peel strength than that of sample 3. In principle, peel strength strongly depends on adhesive thickness, weight fraction of AA, gel content, T_g , the polymer molecular weight and the ratio of surfactant to total monomers.¹⁶ So in this study, the influential factors such as adhesive thickness, weight fraction of AA and the ratio of surfactant to total monomers were maintained invariable. For relatively high gel content, molecular weight and T_g , the sample 3 exhibited a poor ability to flow uniformly and wet the PE substrate surfaces which resulted in a discontinuous adhesion between the adhesive and the PE substrates. For these reasons, the sample 3 showed a poor T-peel strength at low temperature (25°C) with an adhesion failure. Because the

TABLE IV
Gel Content of Samples

Samples	1	2	3	4	4+A	5	5+A
CTA amounts (phm)	0.7	0.5	0.1	0.5 (core) + 0.5 (shell)	–	0.1 (core) + 0.36 (shell)	–
Gel content (wt %)	5.55	5.02	55.97	6.64	9.44	60.50	63.62
Peel strength ^a (g/in.)	65.6	164.0	574.1	212.5	508.5	468.7	623.4

^a The peel strength was determined at 60°C .

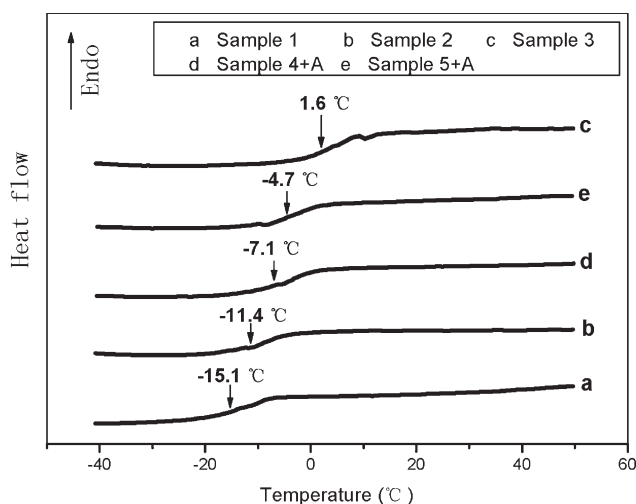


Figure 7 DSC scans of dry adhesives of samples.

sample 1 had the lowest gel content, molecular weight and T_g , it could flow uniformly and wet the PE surfaces. Hence, sample 1 showed the highest peel strength but with a cohesive failure.

As temperature increases, however, those samples have reverse performances (Fig. 8). The peel strength of sample 3 increased with temperature increasing. When the temperature was up to 60°C, sample 3 showed the highest peel strength (574.1 g/in.) than that of samples 1 and 2 (65.6 g/in. and 164.0 g/in. respectively). Given prior knowledge, all samples tested at relative high temperature (60°C) were performed as pressure-sensitive adhesives. It has been known that cohesive strength increases as the gel content increases for pressure-sensitive adhesives.¹⁶ Also, the stiff chains segment of sample 3 could move relatively and wet the surface of the substrates at high temperature. Therefore, the sample 3 exhibited the highest peel strength. On the contrary, T-peel strength of samples 1 and 2 decreased with

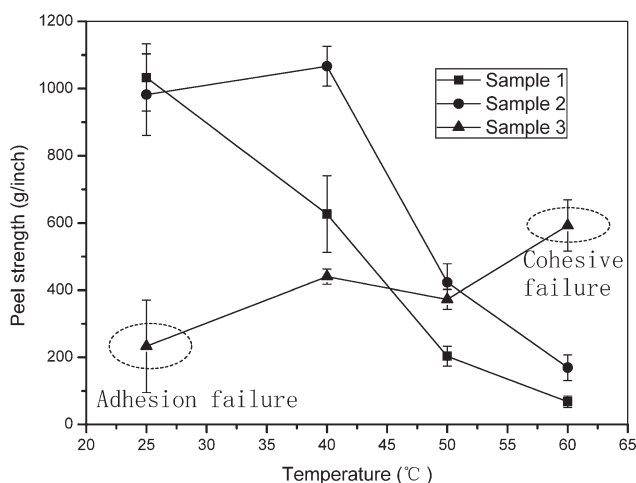


Figure 8 Effect of temperature on peel strength of samples 1-3.

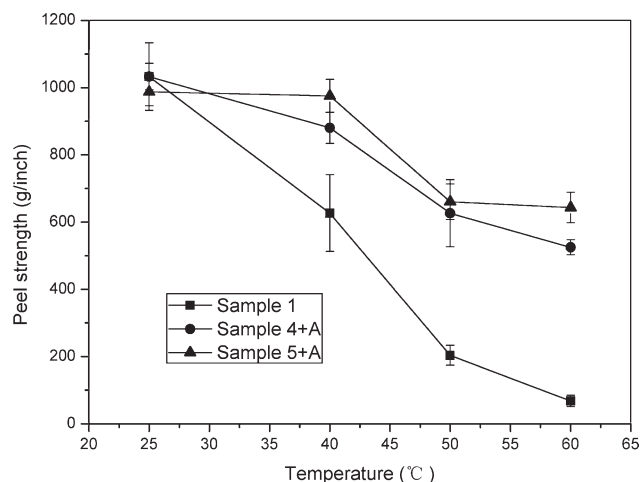


Figure 9 Effect of temperature on peel strength of samples 4+A and 5+A.

increasing temperature. For example, at 60°C, T-peel strength decreased to a very low value. Though the low gel content, molecular weight and T_g contribute LAs to contact with the PE film surface during the bonding phase of the adhesive process, the cohesive strength is too low to resist heat.

The T-peel strength of samples 4+A and 5+A at different temperature are showed in Figure 9. In contrast with samples 1-3, 4+A, and 5+A have core-shell structures due to the multistage polymerization. For the sample 4+A, because of high amount of CTA used at both core and shell polymerization stages, the core and shell were low gel and \bar{M}_w copolymers. Due to the relative low AAEM content used at core stage (0.4 phm) and relative high AAEM content used at shell stage (0.6 phm), the more acetoacetoxy groups were enriched in the shell, which were in favor of crosslinking reaction. Before the crosslinking reactions, sample 4+A with low gel and low \bar{M}_w copolymers was able to wet the surfaces of PE substrates. Then, postcrosslinking reactions between acetoacetoxy groups and ADH could introduce crosslinking structure to LAs and increase the gel content and the T_g of LAs. Consequently, the cohesion of LAs is improved and the heat resistance of sample 4+A is enhanced.

For the sample 5+A, the core was copolymer with relatively high gel and molecular weight, but the shell latex was relatively low gel content and molecular weight copolymer with acetoacetoxy groups. Before the crosslinking reactions occurring, the low gel and \bar{M}_w copolymers within the shell provided high initial adhesion. After postcrosslinking reactions, crosslinking structures were caused by the postcrosslinking reactions of the acetoacetoxy groups within the shell polymer chains with ADH to enhance the copolymer cohesion. In addition, other crosslinking network structure occurred through the

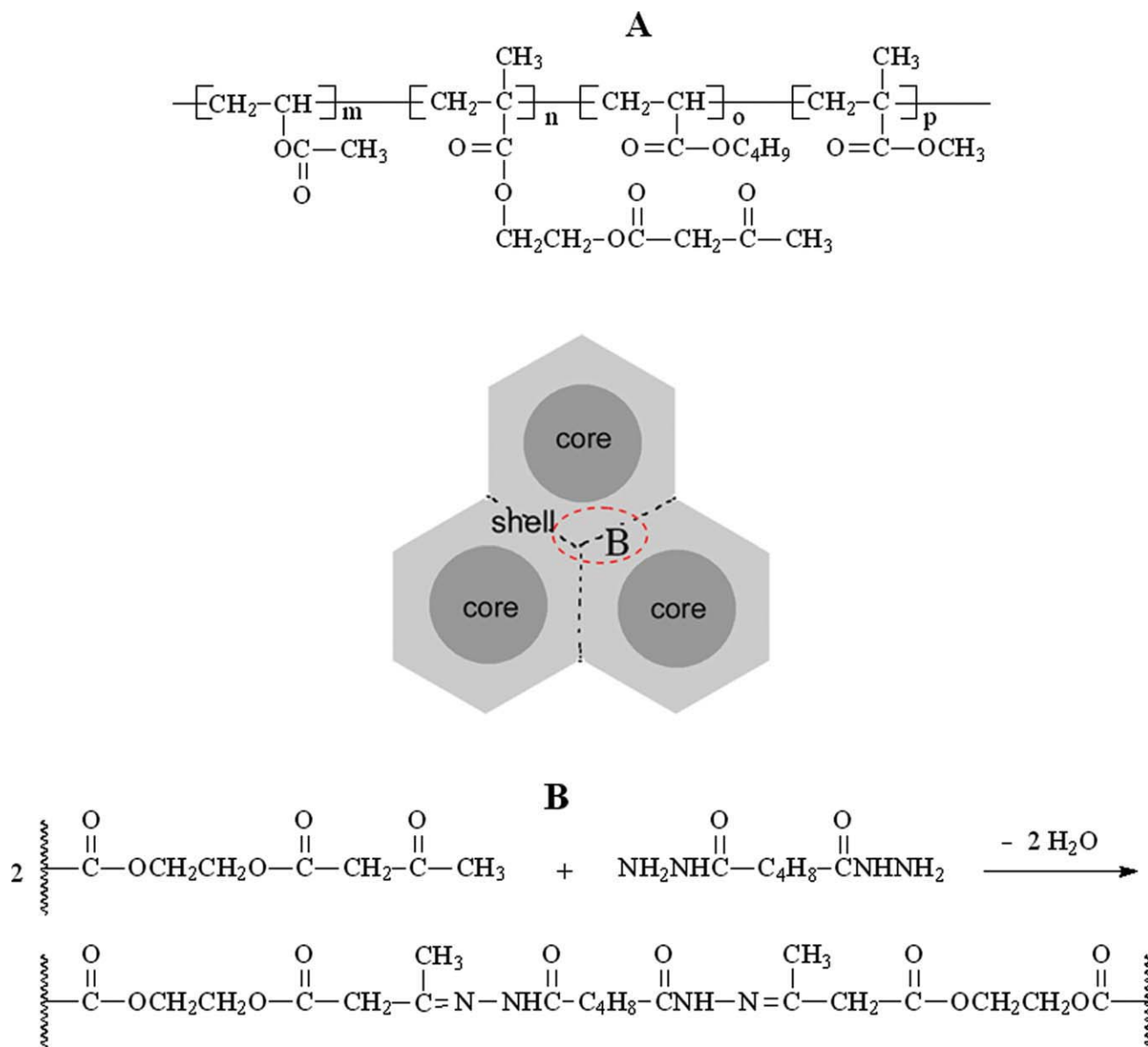


Figure 10 The crosslinking mechanism of the samples 4+A and 5+A. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

entanglements between high \overline{M}_w copolymer chains in core and shell. Therefore, due to the two kinds of crosslinking networks from the crosslinked polymer chains and the entanglements between polymer chains, the gel content of sample 5+A increased and the cohesion strength was enhanced. Thus, sample 5+A possessed an outstanding heat resistance properties. The structure and the crosslinking mechanism were sketched as shown in Figure 10.

CONCLUSION

This work has demonstrated that the effect of particle structure of emulsion LAs on the adhesion properties (peel strength and heat resistance). It was

found that the samples 1 and 2 synthesized with the high CTA contents (0.7 and 0.5 phm, respectively) displayed high peel strength (1032.9 and 982.1 g/in., respectively) at 25°C but with poor heat resistance property (65.6 and 164.0 g/in., respectively) at 60°C due to the low \overline{M}_w and absence of crosslinking structure. Conversely, the sample 3 prepared with low CTA content (0.1 phm) exhibited low peel strength (232.8 g/in.) at 25°C, but relatively high heat resistance property (574.1 g/in.) at 60°C, due to the relatively high \overline{M}_w and the crosslinking network caused by entanglements between polymer chains. The structured particle design and postcrosslinking were approaches to combine these advantages of the samples 1–3 in an effective way. Through structured particle design, sample 4+A possessed low \overline{M}_w

copolymers both in core and shell and reactive acetoxy groups within the core and shell copolymers, while sample 5+A contained high \overline{M}_w and gel copolymers in core but low \overline{M}_w copolymers with enriched reactive groups in shell. Before crosslinking reactions, the low \overline{M}_w copolymers with low T_g and gel content were capable of flowing uniformly and wetting the surface of substrate. After crosslinking reactions, the crosslinking network structures resulted from the crosslinked polymer chains and the entanglements between polymer chains could improve the heat resistance property of LAs. So the samples 4+A and 5+A were observed with high peel strength (1032.9 and 987.2 g/in., respectively) at 25°C and high heat resistance properties (508.5 and 623.4 g/in., respectively) at 60°C.

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