

고분자 분산제를 이용한 Core-shell 수성 감압점착제

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Waterborne Core-shell Pressure Sensitive Adhesive (PSA) Based on Polymeric Nano-dispersant

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요약: 유연한 식품포장필름에 사용되고 있는 드라이 라미네이션용 유성점착제를 대체하기 위해, 고분자 분산제를 사용하여 유화하는 방법으로 수성 감압점착제를 친환경적으로 설계하였다. 유화중합에서 널리 사용하는 저분자량의 계면활성제는 물성의 변수로 작용해 왔다. 본 연구에서는 먼저 용액중합으로 polymeric nano-dispersant (PND)를 제조하고, 이 PND 입자들의 분산제를 micelle seed로 이용하여 core-shell grafted acrylic 점착제를 합성하였다. 이때 입자의 바깥층(shell)과 입자내층(core)의 T_g 를 달리하여 얇은 필름의 점착조건인 초기점착력과 유지력의 균형을 이루도록 설계하였다. 최적화된 시험군 합성 점착제의 물성을 국내외 제조사에서 개발된 연구시료들과 비교분석하여, 점착제로서의 물성을 검토하였다. 물성 비교 결과, 본 연구에서 설계 합성한 저분자량의 계면활성제를 대체 사용한 고분자 나노분산제 기반 core-shell 점착제가 연포장에 적합한 점착물성을 나타냄을 확인하였다.

Abstract: An environmentally friendly water-based pressure sensitive adhesive (PSA) was designed in an attempt to replace the solvent-based adhesive for dry lamination used in flexible food packaging films. Instead of using a low molecular weight surfactant, which may have variable material properties, a high molecular weight dispersant was used for emulsification. A polymeric nano-dispersant (PND) was synthesized using solution polymerization, and it was used as a micelle seed in the surfactant, resulting in the synthesis of a core/shell grafted acrylic adhesive. The shell and core exhibited different T_g values, so that the initial adhesion strength and holding power were complemented by the film's flexibility, which is required to provide good adhesion of thin films. Results showed that the PSA designed in this study using the PND instead of traditional low molecular weight surfactant had adhesive properties applicable to the flexible packaging with appropriate tack.

Keywords: pressure sensitive adhesive (PSA), dry laminate, flexible food packaging film, core-shell, polymeric nano-dispersant (PND)

1. Introduction

Water-based acrylic pressure sensitive adhesives (PSAs) are generally manufactured by mixing incorporating several acrylic monomers in desired ratio using water and emulsifier for emulsion polymerization. These emulsion resins form films which are mostly colorless and transparent. They are commonly used as the base resins in paint and lamination adhesives due to their

good resistance to weather, water, alkalis, contamination, and chemical reactions[1]. An emulsifier is required as a supplemental agent in water-based acrylic emulsion polymerization to obtain the stable and desired particle sizes [2-4]. However, its use is problematic in existing emulsion polymerizations. Conventional emulsifiers have low molecular weights and water-soluble functional groups, and they lack affinity with high molecular weight resins, causing them to migrate to the surface during film formation. They also may lower adhesive strength and water resistance and, by absorbing water or moisture,

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produce whitening phenomenon over time. Surface migration of the adhesive substance tends to leave a residue on the surface upon removal[5].

Several methods have been proposed to address these problems. Using a polyfunctional cross-linking agent and metal ion cross-linking agent was found effective in increasing water resistance. Copolymerization of monomers containing carboxyl group and acrylic ester, and adding methacrylic acid, ethylene glycol, and ethylene diglycidyl ether as cross-linking agents were also reported[6]. These substances, however, led to a decrease in adhesive strength, which made them unsuitable for use as pressure sensitive adhesives.

Recently, industries have made efforts to design non-toxic or low-toxicity products for protection of the environment on the global scale. Water-based adhesives, typical example of such efforts, usually consist of a single component, which renders good homogeneity, resistance to oxidation, and durability. However, water-based adhesives have relatively low adhesive strength compared to the solvent-based adhesives and consume large amounts of energy due to low drying rate during film formation[7,8]. Some studies found a lower time dependence of adhesive strength and improved resistance to water and heat using polymeric emulsifiers, thereby enhancing storage stability[9,10].

Non-aqueous dispersion (NAD) polymerization, which can compensate many shortcomings of water-based polymerization and lower the toxicity of solution polymerization, is gaining considerable attention as an environmentally friendly method[11,12]. However, it is noted that there are also developments to make the solution polymerizations more environmentally friendly by employing aliphatic solvents instead of aromatic ones[13-15].

In general, the particles in the aqueous dispersion of an acrylic emulsion have a composite structure of a hard core and soft shell, which enhances the holding power and physical properties of the aqueous dispersion. Non-aqueous dispersion is similar to solution polymerization in that a monomer is dissolved in a solvent. At the same time the phase separation occurs during polymer formation and a dispersed phase of graft polymers is produced, which works as a stabilizer[16]. The acrylic emulsion adhesive derived from a polymeric surfactant exhibited a much greater water resistance, and its adhesive strength varied much less with time compared to that of existing surfactant[17].

It has also been reported that the emulsion colloid containing aqueous dispersion of hydrophilic acrylic acids showed good stability[18-22]. Viscoelastic effects influenced physical properties of the dried films to varying degrees such as diffusion and barrier properties.

In our investigation of emulsion polymerization the surfactant was replaced with a micelle seed polymeric nano-dispersant (PND), which was synthesized via solution polymerization using alcohol solvent. Alcohol is considered to be more environmentally friendly than existing volatile organic compounds, and the micelle seed polymer assumes the role of the emulsifier surfactant. Material properties such as adhesive characteristics, the particle size and distribution, the glass transition temperature, and storage stability were evaluated. The performance of the pressure sensitive adhesive designed in this study for flexible packaging was examined.

2. Experimental detail

2.1. Materials

Syntheses of PND and PSA were performed using the acrylic monomers including methyl methacrylate (MMA), *n*-butyl acrylate (BA), methacrylic acid (MAAc) and acrylic acid (AAc). They were purchased from Duksan Pure Chemicals (primary reagent grade). Trimethylol propane triacrylate (TMPTA, M-300, Miwon Co.) was used as a functional monomer. Isopropyl alcohol (IPA, Duksan Pure Chemicals) was used as the solvent. Benzoyl peroxide (BPO, Duksan Pure Chemicals) and *tert*-amyl peroxyvalate (*t*-APP, 75%, Seki Arkema) were initiators for the PND synthesis. Ammonium persulfate (APS, Duksan Pure Chemicals) was used as initiator for emulsion polymerization of with shell and core. Dodecyl mercaptan (Seki Arkema) was used as chain transfer agent (CTA), and ammonium hydroxide (NH₄OH, Duksan Pure Chemicals) was used as neutralizer throughout the work. All reagents were used as supplied without further purification.

2.2. Syntheses of PND and Core-shell Graft Acrylic PSA

For the PND synthesis[23,24] BPO or *t*-APP was added to the reactor containing IPA solvent at 85°C according to the formulation in Table 1.

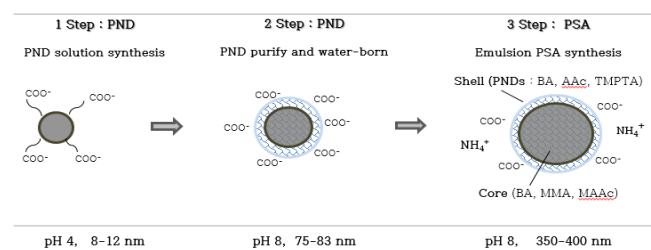
The previously prepared monomer mixture that was then fed slowly to the reactor. After the feeding was complete, the mixture was ripened and then cooled to

Table 1. Recipe for Solution Polymerization of PND

	PND-1		PND-2		PND-3	
Comonomer ^a	MMA	4.5	BA	9	BA	9
	BA	4.5	AA	3	AA	3
	AA	3	TMPTA	1	TMPTA	1
	TMPTA	1				
Solvent	IPA	66.1	IPA	66.1	IPA	66.1
Initiator	<i>t</i> -APP	1.5	BPO	1.5	<i>t</i> -APP	1.5
Neutralizer	NH ₄ OH	1.4	NH ₄ OH	1.4	NH ₄ OH	1.4
	water	18	water	18	water	18

a : total comonomer content was 13 wt% with regard to the solvent (IPA)

* amount in ml

**Figure 1.** PND and PSA Polymerization Process.

room temperature after checking the residual monomer. Solvent was removed from the polymer dispersant at 35°C under vacuum, and the acid number was measured.

Low molecular weight substances were removed from the PND by precipitation with a fivefold excess of *n*-heptane, and the PND was allowed to stand until stabilized. Upon filtering and separation pure PND was obtained by vacuum concentration and dried to constant weight. The dried polymer was re-dispersed in water to yield a solution of 30% solid content, which was then used as a supplemental agent as the micelle seed in the emulsification of the core/shell grafted acrylic PSA. Depending on the comonomer composition and the initiator, three different types of PND were synthesized, each of which showed different T_g . PND-1 could be pulverized, whereas PND-2 and PND-3 showed low T_g s, and thus they were liquefied. Flexible pressure sensitive adhesive was manufactured by grafting acrylic monomers onto the PND micelle seeds in emulsion polymerization[25,26].

In order to balance the physical properties and shorten the drying time of the final adhesive, the PSA composition was adjusted to have the final solid content of 48%. Monomers in the core and shell were mixed at

different ratios to provide different T_g values, and the shell was designed to exhibit the properties of flexible adhesives. The amount of the PND emulsifier (30% aqueous solution) was 1.5 times of the monomer mixture by weight.

Into the shell monomer mixture 30% PND and water were mixed, and the temperature was increased to 85°C. 10 g of the core monomer mixture previously prepared and 0.33 g of diluted APS catalyst were injected to the shell mixture under nitrogen. After 15 min 1 g of diluted APS and 0.1 g of NH₄OH (28%) were further introduced to form micelle seeds. Thereafter, the remaining core monomer mixture was fed evenly over 140 min.

At the same time, 1.2 g of diluted APS and 0.12 g of NH₄OH (28%) were continuously added for 60 min with the remaining core monomer mixture.

Once reaction was complete, the contents were heated to 87°C and allowed to ripen for 60 min. The pH was adjusted to 8. After cooling to room temperature, the emulsions was filtered obtain the core-shell PND grafted acrylic PSA. Figure 1 shows PND and PSA polymerization process.

2.3. Characterization of Material Properties

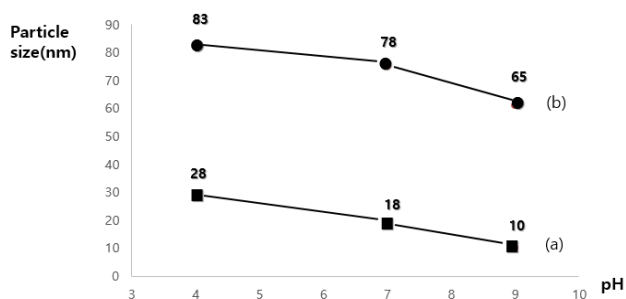
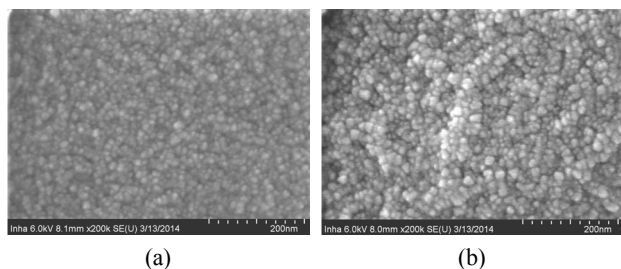
The glass transition temperature was measured after drying by DSC (NETZSCH Thermal Analyzer, DSC404F1). The T_g of the adhesive synthesized in this study was formulated to be around -20°C. The average molecular weight and the molecular weight distribution were measured by GPC (Waters GPC system) with a guard column attached, using THF as solvent. Particle morphology was characterized using SEM (Hitachi FE-SEM/EBSD S-4300SE) and TEM (Phillips CM200).

Table 2. Effect of Initiator Molecular Weight and Particle Size of PND

Initiator	BPO(PND-2)		<i>t</i> -APP(PND-3)	
	(a)	(b)	(a)	(b)
Mn	3,303	4,029	2,177	3,732
Mw	6,492	9,583	4,120	8,358
PDI	1.96	2.38	1.89	2.2
particle size (nm)	11	53	8	75

(a) : upon synthesis

(b) : after Refining and re-dispersion

**Figure 2.** Effect of PND Particle size in accordance with the type of catalyst (a) PND-2 Particle size (■), (b) PND-3 Particle size (●).**Figure 3.** Honeycomb dry film SEM morphologies of (a) PND-3 and (b) PND-3 grafted PSA stabilized at pH 8.

Particle size and zeta potential of PND and PSA were measured by Electrophoretic Light Scattering & Zeta Potential Analyzer (OTSUKA ELS-8000). To investigate the adhesive properties PSA was coated onto a 1.5 mil oriented polypropylene (OPP) film to obtain a film thickness of 0.2 mil. The laminated film was dried in an oven at 105°C for 3 min to reduce the thickness to about 0.1 mil by removing the solvent in the oven. The adhesive was placed on another 1.5 mil cast polypropylene (CPP) or OPP film, and pressure was applied with a rubber roller. The adhesion properties were examined by applying PSA between two thin polypropylene films. The OPP-OPP and OPP-CPP layers were tested with the roller set to a pressure of about 20 psi and a

temperature of 38°C. The t-peel adhesion characteristics of the laminated film were measured at 25°C with a sample of 25.4 mm width measured according to ASTM D3330. The viscosity was measured at 25°C and 20 rpm using Brookfield viscometer. The acid number measurement of PND was based on ASTM D3643-2010[27].

3. Results and Discussion

3.1. Effect of Initiator on the Material Properties of PND

When the PND was synthesized using BPO as the catalyst, it required high reaction temperature, which destabilized its reactivity. The mean particle size was 11 nm with a distribution of 5~50 nm. A large amount of foam occurred during concentration, which made the handling difficult, and the prepared PND was discolored to yellow. The number average molecular weight of the dispersant before and after removal of the low molecular weight particles was about 3,300 and 4,000 respectively. Use of *t*-APP as catalyst resulted in lower reaction temperature and better reactivity, making it advantageous for the PND synthesis. The mean particle size was 8 nm with a narrow distribution of 5~55 nm. Overall, the particle size was small, and there was no foam and little gel formation, making it easier to work with. There was also little discoloration of the PND during reaction. The number average molecular weight of the dispersant after synthesis and after removal of low molecular weight particles was about 2,200 and 3,700, respectively. Overall, *t*-APP was found to be more suitable based on its higher reactivity, less discoloration, less foam formation, the molecular weight and the particle size. In case of PND-3, the particle size after synthesis was 8.9 nm while it was 75.3 nm after re-dispersion with dilution at 30%. Table 2 shows the effect of initiator on the molecular weight and particle size of PND.

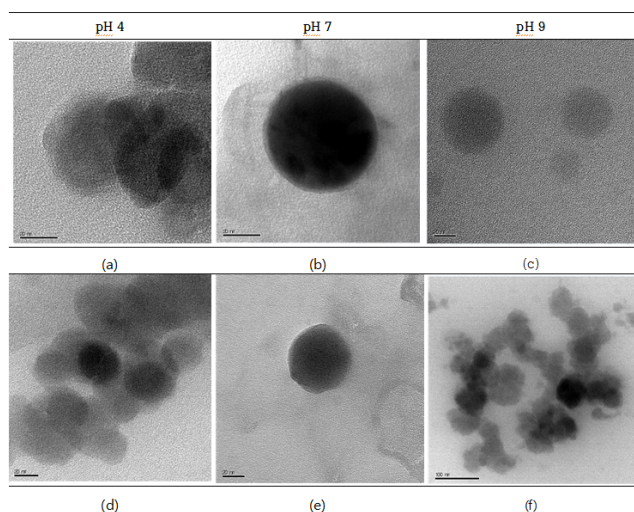


Figure 4. Effect of pH on particle size and stability : (a)~(c) PND-2 polymerized by BPO, and (d)~(f) PND-3 polymerized by *t*-APP.

*Scale bar : (a)~(e) 20 nm, (f) 100 nm

3.2. Effect of pH on the Particle Stability of PND

To assess the particle stability of PND as a function of pH and the degree of dispersion, zeta potential measurement was employed at pH values of 4, 7, and 9 after the purified PND was diluted to 30%. When BPO was used as the catalyst, the dispersion was stable at pH 4 with a zeta potential of -48.79 mV and the mean particle size was 38.6 nm. At pH values of 7 and 9, the zeta potentials of lower than were -40.72 mV and -36.88 mV, respectively, and the dispersant gradually dissolved to become a transparent, yellowish solution. When *t*-APP was used as the catalyst, the dispersion was stable at pH 7 with a zeta potential of -69.49 mV and the mean particle size of 17.7 nm. However at pH values of 4 and 9, precipitation followed immediately, which made the solution translucent, generating a fair amount of foam and the solution proved to be unstable. At pH between 7 and 8, the dispersion was stable and formed a milky dispersion with little foam and without discoloration. The polymer dispersant using the *t*-APP catalyst was found to be more sensitive to pH. Thus, pH of the PND-3 grafted PSA was adjusted to 8. Figure 2 presented effect of PND particle size in accordance with the type of catalyst.

The core-shell PSA was designed to incorporate acrylic acid and methacrylic acid and a stable electrostatic colloid was obtained under the high values of pH due to negatively charged carboxylic acids. Thus, stable par-

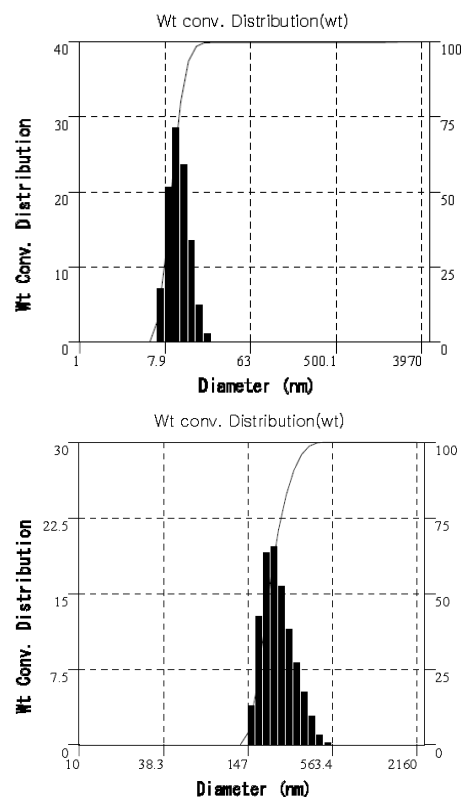


Figure 5. Particle size distribution of (a) PND-3 and (b) PND-3 grafted acrylic PSA.

ticle dispersion with a zeta potential of lower than -40 mV was obtained at pH 4 when BPO was used as catalyst and at pH 7~8 when *t*-APP was catalyst.

Figure 3 shows the SEM particle image of PND-3 and PND-3 grafted PSA stabilized at pH 8. The effect of pH on the particle morphologies of PND-2 and PND-3 observed by TEM is presented in Figure 4.

3.3. Characteristics of PND and PND grafted acrylic core-shell PSA

The T_g of PND-1 was 16°C, and that of both PND-2 and PND-3 was -23°C. Acid value ranged between 80~120 (KOH mg/ Purified PND g). As discussed above, PND-3 was found to be suitable for the formation of the flexible dispersant required in this study.

As the carboxylic acids on the PND particle are hydrophilic they are located on the surface of the PND particle. When acidic monomers or hydrophobic monomers are introduced, they tend to diffuse into the core of the particles. Thus the core-shell particles grew as the polymerization of core monomers proceeds.

The particle size of the PND-3 grafted PSA was

Table 3. Comparison of Physical Properties of Various PSAs

	PND-3 graft acrylic PSA	Product A	Product B	Product C
TS (%)	48%	48%	42%	42%
pH	8	7	7	7
Adhesion Strength (g/in)	340	395	258	185
Molecular Weight	280,000	-	-	-
viscosity (cps)	1,000	1200	1000	500
Particle size (nm)	362	860	325	210
T_g (°C)	-18	-25	-10	-5

found to be 200~500 nm with the average size of about 362 nm. The molecular weight of PND-3 grafted acrylic PSA was 280,000, and the glass transition temperature was -18°C. The adhesive force was 340 g/in, and adhesive properties were well balanced with flexibility, and little change in properties with time. The solid content was designed to be 48% allowing for the drying speed. Figure 5 shows the particle size distribution of the PND-3 and PND-3 grafted acrylic PSA.

The PSA particles produced in this study formed core-shell structure. Upon drying of the PSA particles, the surface of the film showed honeycomb morphology, as shown in Figure 3. Neighboring particles created void space which could affect the mechanical and adhesive properties[28].

When pH of the PSA emulsion is low, abundant carboxylic acids on the particle surface can form hydrogen bond with neighboring carboxylic acids. Therefore film formation is possible; however, it becomes highly adhesive with a low drying speed. On the other hand, in the case of high values of pH, particles of functional monomers and comonomers will be ionized with carboxylic acid and they interact with counterions that would lead to low adhesive strength.

In this study, PND-3 showed low pH and was soft. When PND-3 was dispersed and neutralized, the particles became stable. pH of the PND-3 grafted acrylic PSA was kept at 8 to maintain stability of the PSA. Wang et al.[28] studied the characteristics of the two important neutralizers, NaOH and NH_4OH . Na^+ ions remained on dried films, but NH_4^+ ions, when exposed to heat, evaporated. NH_4OH allowed a quick drying speed and it was found effective in providing low adhesive strength. Based on their result, pH value of our PSA was set at 8, and NH_4OH was chosen to be the neutralizer. The adhesive strength prior to neutralization was 520 g/in,

and after neutralization it was reduced to 340 g/in.

3.4. Performance of PND grafted acrylic core-shell PSA

The adhesive was manufactured by synthesizing the core-shell graft copolymer using PND which acted as the micelle seed instead of the conventional emulsifier. The core-shell PSA particles synthesized by emulsion grafting were very stable. Copolymers that contained carboxylic acid showed pH dependent properties. Under acidic conditions, the hydrogen bonds in MAAc retain water, which lowers the drying rate of the PSA. If the pH is increased, the hydrogen bonds are broken and the COO^- groups in MAAc become neutral dipoles, balancing the counter-ions and increasing the drying rate. Thus, the intermolecular effects accelerate drying. Wetting and leveling on the substance surface are enhanced as well, which allows for film formation with even a small amount of lamination.

The final emulsion adhesive based on the PND grafted acrylic PSAs synthesized in this study had an adhesive strength of 250~400 g/in as flexible film. It showed a reasonable adhesive strength and flexibility for the OPP and CPP films.

The performance of the commercial products of foreign and sample domestic manufacturers with various T_g s was analyzed to compare with our results. Table 3 lists comparison of physical properties of our PND-3 grafted acrylic PSA sample and three commercial products (Product A, B and C). All the PSAs in the table are ionic. Product A had a relatively high adhesive strength, and was unsuitable for the flexible OPP and CPP packaging films. However, it showed better properties for industrial films such as PET and nylon. Product A exhibited time-dependent changes and it was destroyed at low temperatures. Products B and C showed tunneling behavior. PND-3 grafted acrylic adhesive synthesized in

this study did not show any film destruction, tunneling, nor time-dependent property changes and it showed appropriate flexibility and adhesive strength.

4. Conclusions

Replacement of the surfactant with the PND is expected to reduce the possible transfer of chemicals to food in food packaging, which makes the current adhesive system more environmentally friendly.

The PND-3 grafted core-shell emulsion PSA showed high drying speed, stable dispersion at pH values of 8 and above, and small particle sizes, which allowed for thinner lamination. Due to its wetting and leveling properties, it may be applied to plastic films, which have a low surface tension, with little transformation over time. It also meets the material property requirements of flexible adhesives. Sample commercial products, which are based on conventional emulsion, showed problems of film degradation due to inflexibility and material property changes over time. Although it is difficult to examine the physical properties of 0.2 μm thick adhesive laminate, the pressure sensitive adhesive system exhibits a dry lamination property very close to that of the conventional solvent-based adhesive system. It is expected that a gradual increase in the demand of environmentally friendly adhesives and import substitution effect and lamination materials will generate more interest in developing waterborne adhesives further.

Acknowledgements

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