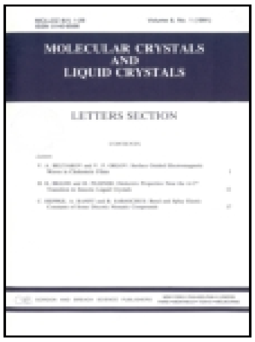

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Synthesis of Thermally Stable Waterborne Acrylic Pressure Sensitive Adhesives (PSAs) for Application to LCD Devices

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The new thermally stable acrylic pressure sensitive adhesives (PSAs) were synthesized by pre-emulsion addition method, characterized by FT-IR spectra and differential scanning calorimetry (DSC), and evaluated their physical properties based on reactive emulsifiers and tackifiers. Experimental Tg of PSAs with different monomer compositions was similar to its theoretical values. The PSAs with reactive emulsifier showed higher mechanical and thermal properties than those with conventional emulsifier. The novel thermally stable acrylic PSA synthesized from 2-ethylhexyl acrylate (2-EHA) and butyl acrylate (BA) as main monomers, and methylmethacrylate (MMA) and acrylic acid (AAc) a cohesive monomer, and reactive emulsifier and tackifier, showed excellent physical properties such as initial, moisture and heat resistant peel strengths, which are considered to be one of the most important properties to be applied for liquid crystalline display (LCD) devices.

Keywords pressure sensitive adhesives (PSAs); reactive emulsifier; tackifier; LCD; acrylic polymer; pre-emulsion addition method

Introduction

Pressure sensitive adhesives (PSAs) don't require drivers like water, solvent, light or heat, and it can adhere to the surface of other object in short time with a small pressure like finger pressure, and because it is a cohesive material, it is easily detached without contaminating the adhered object.[1–3] Because PSAs are polymeric materials, tack, peel and shear strengths are influenced by the properties of the polymer, such as copolymer composition, microstructure, molecular weight and distribution as well as glass transition temperature (Tg). By careful selection of the chemical composition, the physical and rheological properties of PSA can be controlled and tailored to suit the needs of a particular

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application. Acrylic PSA, transparent acrylic copolyester material without color, is not yellowed even when it is exposed to the sun light.[4, 5] Acrylic PSAs had been applied for a wide range of industries especially, optical film adhesion in LCD due to their low price and a relatively simple manufacture process as well as their excellent anti-oxidant properties, weatherabilities, oil-resistance, and thermal stabilities by adjusting the functional monomer compositions.[6–10] Even though PSAs used in optical film adhesion covers small portions less than 5% in total LCD production cost, they strongly affect LCD performance.[11] Mostly, acrylic PSA has been used in LCD to adhere the optical film onto LCD panel and prevent shrinkage or expansion of optical film on LCD panel under high temperature and high humidity environment.[12] Therefore, there is a strong need in creating such types of acrylic PSAs with high thermal stabilities, and moisture and heat resistances for LCD devices. In this study, high thermally stable acrylic PSAs were synthesized from various reactive emulsifiers and tackifiers by pre-emulsion addition method and formulated to obtain the optimal physical properties for LCD devices.

Experimental

Synthesis of novel thermostable acrylic PSA

It has been generally known that alkyl (meth)acrylate with 4∼17 carbons are suitable for the synthesis of PSA, and 2-EHA, BA, and IOA (isooctyl acrylate) are typically used as main monomers. However, due to their low glass transition temperature (Tg) and cohesiveness, they were often copolymerized with other functional monomers, leading to higher Tg and better cohesiveness. NP (Nonyl phenol)–free reactive nonionic/anionic emulsifiers and rosin type / C_5 type tackifiers with excellent physical properties were used to synthesize novel thermostable acrylic PSAs, while minimizing other factors. These functional monomers, emulsifiers and tackifiers listed in Table 1 were obtained from Aldrich Co. (USA) and LG Chem Co. (Korea) and Wuzhou Co. (China) and Nipon Zeon Co. (Japane) and used without purification.

Various kinds of PSAs were synthesized to obtain the optimal PSAs, by formulating BA and 2-EHA as main monomers, MMA and AAc as cohesive monomers, equivalently, and by changing the composition of reactive emulsifiers and tackifiers, and finally evaluated their adhesiveness, heat resistance, and moisture resistance, which are the core properties as PSA for LCD devices.

The polymerization procedure was typically followed pre-emulsion technique which indicates the monomers used were emulsified prior to the addition to the reactor making the reactions more stable, with the polymerization apparatus shown in Fig. 1.

Briefly, deionized water, certain amount of emulsifier, and sodium bicarbonate were added to a round-bottom flask equipped with a nitrogen gas inlet, reflux condenser, agitator, and minor amount pump. The pre-emulsion prepared from deionized water, certain amount of emulsifier, and potassium persulfate (KPS) as a initiator in beaker, followed by the addition of monomers was injected slowly to the above solution through metering pump with constant addition speed at 85°C for 5 h. The polymerization was allowed to react for an additional 3 h with continuous stirring. polymerization process shown in Fig. 2.

Calculation of glass transition temperature (Tg)

Glass transition temperature (Tg) is the temperature when segmental micro-brownian motion begins in amorphous regions of polymer. Theoretical Tg can be obtained by mass

Table 1. Monomers, emulsifiers and tackifiers used in this study

Monomer	Abb	Chemical Structure	Tg(°C)
2-Ethylhexyl acrylate	2-EHA	$CH_2{=}CHCOOCH_2CH(C_2H_5)C_4H_9$	−70
Butyl acrylate	BA	$CH_2{=}CHCOOC_4H_9$	−54
Methyl methacrylate	MMA	$CH_2{=}C(CH_3)COOCH_3$	105
Acrylic acid	AAc	$CH_2{=}CHCOOH$	106
Tackifier	Abb	Chemical Structure	Type
	100F	$HOCH_2C(CH_2OH)_2CH_2OH$	Rosin
	A-100	$-CH(CH_3)CH(C_5H_{11})CHCH_2CH(CH_3)$ $CH(CH_3)CH_2CH_2-$	C_5
Emulsifier	Abb	Chemical Structure	Type
	S-1	$CH_2{=}CHCH_2OCH_2\ ROCH_2CH(OX)_nOH$	Nonion
	S-2	$CH_2{=}CHCH_2OCH_2\ ROCH_2CH(OY)_nOH$	Nonion
	S-3	$CH_2{=}CHCH_2OCH_2\ ROCH_2CH(OZ)_nOH$	Nonion
	S-4	$ROCH_2CH(OCH_2CH_2)_nOH$	Nonion
	S-5	$CH_2{=}CHCH_2OCH_2\ ROCH_2CH(OX)_nOSO_3$ NH_4	Anion
	S-6	$CH_2{=}CHCH2OCH2\ ROCH_2CH(OY)_nOSO_3$ NH_4	Anion
	S-7	$ROCH_2CH(OCH_2CH_2)_nOSO_3NH_4$	Anion

proportion or mole proportion methods from the monomer compositions. Fox equation based on mass proportion method was used in this study to obtain Tg as follows. [13, 14]

$$1/Tg = W_1/Tg_1 + W_2/Tg_2 + ... + W_i/Tg_i$$

where, W_1, W_2, W_i indicate the mass proportion and Tg_1, Tg_2, Tg_i indicate the Tg of independent homopolymers, respectively.

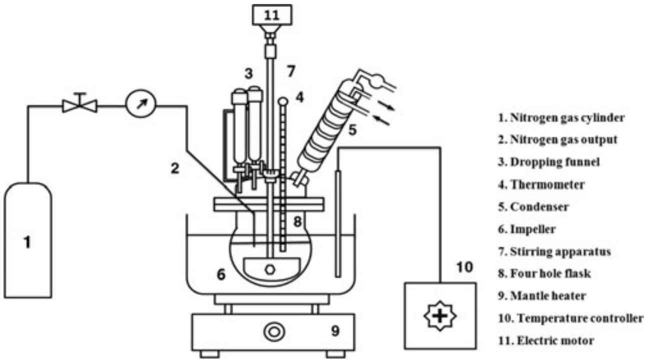

Figure 1. Polymerization apparatus used in this study.

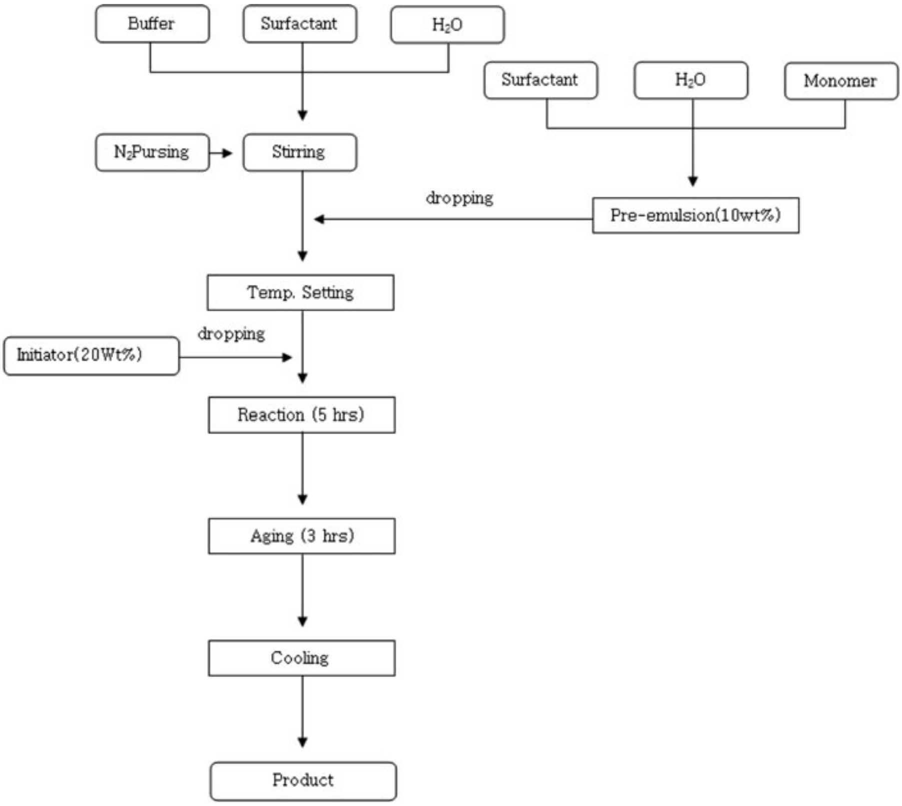

Figure 2. Schematic diagram for the polymerization process.

Measurements

The structures of synthesized acrylic PSAs were identified using JASCO FT-IR 6200 spectrophotometer with a wave range of 4,000∼400 cm^{-1}. Differential scanning calorimetry (DSC) was carried out in a DuPont 910 thermal analyzer with a heating rate of 10°C/min in nitrogen atmosphere ranging from −80 to 20°C.

Polyethylene terephthalate (PET) film and SUS 304 were used as substrates to evaluate the physical properties of PSAs as follows. First, the surface coated PET film with synthesized PSA using applicator in 100 μm/wet thickness was dried at 100°C for 4 min and cut in 25 × 150 mm^2 size, followed by the adhesion to SUS 304 substrate by pressing 3 times with 2 kgf pressure using a hand roller. The universal testing machine (GT-A170006 or AI700S) at cross-head speed of 50 mm/min was used to evaluate various types of peel strengths, such as initial, moisture, and heat resistant peel strengths. Initial peel strength was measured afterthe fabricated sample specimens were kept for 3 min at 25°C. The fabricated specimens first stabilized at 25°C for 72 h were kept at 80°C for 72 h for heat resistant peel strength, and at 40°C under 95% relative humidity for 72 h prior to the evaluation of moisture resistant peel strength.[15]

Results and Discussion

The FT-IR spectra (Figure 3) of acrylic PSAs based on 2-EHA and BA as main monomers with functional monomers such as MMA, with reactive and conventional emulsifier, with

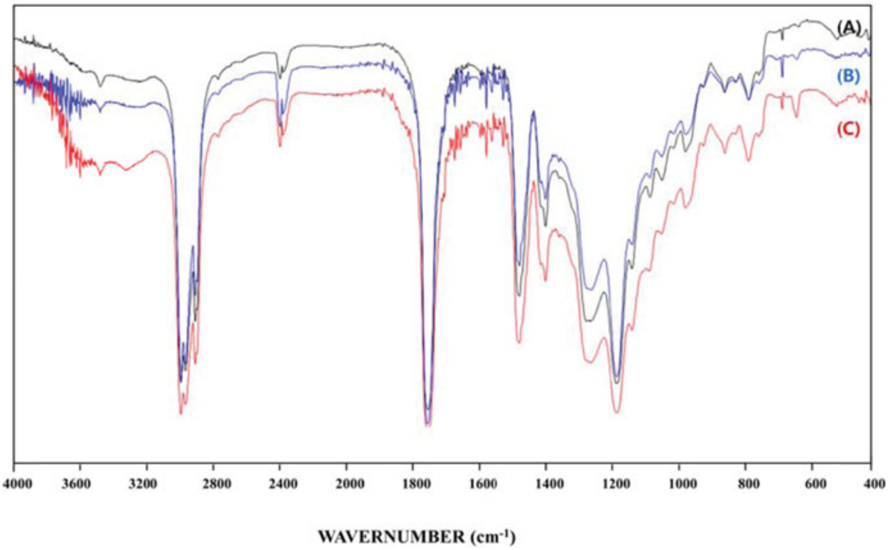

Figure 3. FT-IR spectra of acrylic PSAs with different emulsifier and tackifier. (A) reactive emulsifier(NA-2), (B) conventional emulsifier(C-E), (C) tackifier(T-4).

tackifier indicated characteristic absorption peaks at 2900 ~ 2850 cm^{-1} (stretching vibration of aliphatic C—H), 1730 cm^{-1} (stretching vibration of C=O), 1450 cm^{-1} (CH_2 scissoring) with the concurrent disappearance of vinyl group peak at 1680 cm^{-1} (stretching vibration of vinyl C=C).

DSC permits the determination of glass transition temperature (Tg) of the acrylic PSA synthesized from the optimal formulation, 2-ethylhexyl acrylate(2-EHA) and butyl acrylate(BA) as main monomers, and 10 wt% of methylmethacrylate(MMA) as a cohesive monomers, and nonionic / anionic emulsifier, and tackifier. As shown in Figure 4 and 5, the Tg of the PSA was proved to be −51°C, which is relatively good agreement with

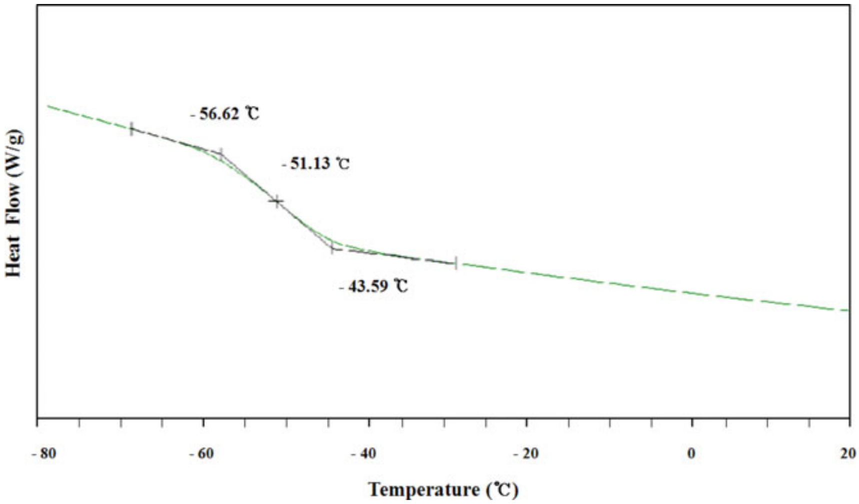

Figure 4. DSC thermogram of acrylic PSA(NA-2).

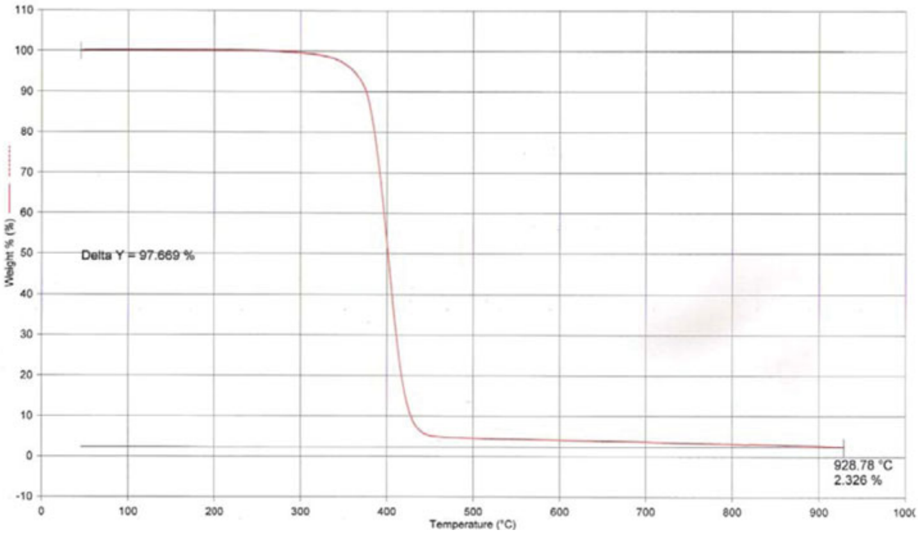

Figure 5. TGA thermogram of acrylic PSA(NA-2).

its theoretical value (−54°C) from Fox equation, and the PSA had similar decomposition temperature with commercial acrylic PSA. Some deviations between the glass transition temperature determined by DSC and theoretical Tg were found, which may be due to remained emulsifier residues, however they are not the major factors affecting on the physical properties of acrylic PSA, because they could act as reactive emulsifiers with polymerizable double bonds.

Various kinds of formulations with emulsifier compositions were used to obtain the optimal PSA for LCD devices. First, the acrylic PSAs with solid content of 56% and theoretical Tg of −54°C based on BA/2-EHA as a main monomer, MMA as a cohesive monomer, AAc as a functional monomer for bonding strength, were synthesized with different NP (Nonyl phenol)–free reactive nonionic emulsifiers, such as S-1, S-2, and S-3, and evaluated their peel strengths, such as initial, moisture and heat resistances. The acrylic PSAs with reactive nonionic emulsifiers (N-1, N-2, N-3), as shown in Table 2, showed relatively low conversion, initial, moisture and heat resistant peel strengths. therefore, overall, the PSAs synthesized based on only reactive nonionic emulsifiers with Tg of −54°C were proved not suitable as those for LCD devices due to lack of tack property.

Second, the acrylic PSAs with solid content of 56% and theoretical Tg of −54°C based on BA/2-EHA as a main monomer, MMA as a cohesive monomer, AAc as a functional monomer for bonding strength, were synthesized with different NP (Nonyl phenol)–free reactive anionic emulsifiers, such as S-5 and S-6, to find the optimal PSAs formulations for LCD devices, and evaluated their bonding strength, moisture and heat resistances. As shown in Table 2, the PSAs based on reactive anionic emulsifiers (A-1, A-2) had generally higher physical properties compared to those based on reactive nonionic emulsifiers in Table 2. However, after PH adjustment, overall, the PSAs synthesized based on only reactive anionic emulsifiers with Tg of −54°C were proved not suitable as those for LCD devices due to the high viscosity and the low rheology with bubble problem.

Third, the acrylic PSAs with solid content of 56% and theoretical Tg of −54°C based on BA/2-EHA as a main monomer, MMA as a cohesive monomer, AAc as a functional

Table 2. Formulation and physical properties of acrylic PSAs with different reactive nonionic and anionic emulsifiers

		N-1	N-2	N-3	A-1	A-2
Formulations (g)	2-EHA	68	68	68	68	68
	BA	21	21	21	21	21
	AAc	2	2	2	2	2
	MMA	9	9	9	9	9
	S-1	4	–	–	–	–
	S-2	–	4	–	–	–
	S-3	–	–	4	–	–
	S-5	–	–	–	4	–
	S-6	–	–	–	–	4
Conversion (%)	94.6	92.9	91.1	99.5	98.7	
Initial peel strength (kgf/25mm)	0.6	0.7	0.7	1.1	1.0	
Moisture resistant peel strength (kgf/25mm)	0.8	0.9	0.8	1.2	1.2	
Heat resistant peel strength (kgf/25mm)	1.0	0.8	1.0	1.3	1.3	

Reaction Conditions : initiator (KPS), 0.3 g; $NaHCO_3$, 0.2 g; H_2O, 80 g; theoretical solid content, 56%; theoretical Tg, −54°C; reaction temp., 85°C; reaction time, 8h.

monomer for bonding strength, were synthesized with different NP (Nonyl phenol)–free reactive nonionic/anionic emulsifiers, such as S-1/S-5 and S-2/S-6, to find the optimal PSAs formulations for LCD devices, and evaluated their bonding strength, moisture and heat resistances. As shown in Table 3, the PSAs based on reactive nonionic/anionic emulsifiers (NA-1, NA-2) had generally higher physical properties compared to those based on reactive nonionic or anionic emulsifiers. Therefore, the PSAs synthesized based on reactive nonionic/anionic emulsifiers with Tg of −54°C were proved suitable as those for LCD devices due to the relatively high tack property.

In order to evaluate the effect of conventional emulsifier and reactive emulsifier on the properties of PSA, both BA and 2-EHA as main monomers were used to formulate acrylic PSAs with solid content of 56% and MMA as a cohesive monomer, AAc as a bonding monomer. As seen in Table 3, at the reactive emulsifier, the synthesized PSA had the highest and most balanced initial, moisture and heat resistant peel strengths, meaning that the novel thermostable acrylic PSA with BA and 2-EHA as main monomers, MMA as a cohesive monomer, reactive nonionic and anionic emulsifier, was the best.

Next, in order to evaluate the effect of tackifier on the properties of PSA, the acrylic PSAs with solid content of 57∼58% and theoretical Tg of −54°C based on BA/2-EHA as a main monomer, MMA as a cohesive monomer, AAc as a functional monomer for bonding strength, were synthesized with different tackifiers to find the optimal PSAs formulations for LCD devices, and evaluated their bonding strength, moisture and heat resistances. As

Table 3. Formulation and physical properties of acrylic PSAs with different both conventional and reactive emulsifiers

		NA-1	NA-2	C-E
Formulations (g)	2-EHA	68	68	68
	BA	21	21	21
	AAc	2	2	2
	MMA	9	9	9
	S-1	2	–	–
	S-2	–	2	–
	S-4	–	–	2
	S-5	2	–	–
	S-6	–	2	–
	S-7	–		2
Conversion (%)	98.9	99.8	99.8	
Initial peel strength (kgf/25 mm)	1.2	1.3	1.0	
Moisture resistant peel strength (kgf/25 mm)	1.3	1.2	0.9	
Heat resistant peel strength (kgf/25 mm)	1.4	1.4	1.2	

Reaction Conditions : initiator (KPS), 0.3 g; $NaHCO_3$, 0.2 g; H_2O, 80 g; theoretical solid content, 56%; theoretical Tg, −54°C; reaction temp., 85°C; reaction time, 8 h.

Reactive emulsifier (R-E) : S-1, S-2, S-5, S-6; Conventional emulsifier (C-E) : S-4, S-7.

Table 4. Formulation and physical properties of acrylic PSAs with different tackifiers

		T-1	T-2	T-3	T-4
Formulations (g)	2-EHA	68	68	68	68
	BA	21	21	21	21
	AAc	2	2	2	2
	MMA	9	9	9	9
	100F (Rosin type)	3	–	–	–
		–	8	–	–
	A-100 (C_5 type)	–	–	3	–
		–	–	–	8
Conversion (%)	94.7	94.8	98.2	98.3	
Initial peel strength (kgf/25 mm)	1.0	1.1	1.2	1.0	
Moisture resistant peel strength (kgf/25 mm)	1.2	1.2	1.2	1.3	
Heat resistant peel strength (kgf/25 mm)	1.3	1.3	1.3	1.4	

Reaction Conditions : initiator (KPS), 0.3 g; surfactant, nonionic(S-2) and anionic(S-6) surfactants were used equivalently; $NaHCO_3$, 0.2 g; H_2O, 80 g; theoretical solid content, 57∼58%; theoretical Tg, −54°C; reaction temp., 85°C; reaction time, 8 h.

shown in Table 4, the PSAs based on C_5 type had generally higher physical properties compared to those based on Rosin type.

In this study, we used initial and moisture/heat resistantpeel strengths to evaluate the physical properties of PSAs formulated with different reactive emulsifier and tackifier compositions. These values can help us to quickly determine which formulation would be potentially workable for LCD industries. Based on the physical properties mentioned above, we decided to pick reactive nonionic/anionic emulsifier and C_5 type tackifier for further formulations because the PSA formulated with reactive nonionic/anionic emulsifier and C_5 type tackifier exhibited the highest and most balanced physical properties among them, which may be more attractive to LCD devices.

Conclusions

Various kinds of PSAs with different reactive emulsifiers and tackifiers were applied for the potential use as adhesives between LCD panel and optical films. Among them, PSA based on both reactive nonionic and anionic emulsifier(NA-2 in Table 3), C_5 type tackifier(T-4 in Table 4) exhibited the optimal physical properties such as moisture and heat resistances with experimental Tg relatively close to its theoretical value. Continuous work involves the practical application to LCD devices including optical properties and the evaluation of environmental friendly properties, as well as the synthesis of antistatic PSA for LCD devices.

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