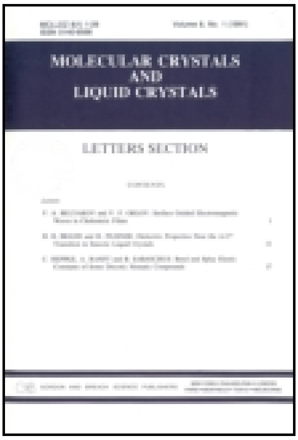

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Synthesis and Properties of Thermally Stable Pressure Sensitive Adhesives for LCD Devices

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Synthesis and Properties of Thermally Stable Pressure Sensitive Adhesives for LCD Devices

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Waterborne acrylic pressure sensitive adhesives (PSAs) were synthesized by pre-emulsion addition method, characterized by FT-IR, ^{1}H NMR spectra and differential scanning calorimetry (DSC), and evaluated their physical properties based on main and cohesive monomers. The waterborne acrylic PSA synthesized from 2-ethylhexyl acrylate (2-EHA) and butyl acrylate (BA) as main monomers, and 10 wt% of methyl methacrylate (MMA) as a cohesive monomer, 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 Acrylic polymer; heat resistance; LCD; pre-emulsion addition method; pressure sensitive adhesive; waterborne

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 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

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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 acrylic monomers by pre-emulsion addition method and formulated to obtain the optimal physical properties for LCD devices.

Experimental

Synthesis of Waterborne 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. These functional monomers listed in Table 1 were obtained from Aldrich Co. (USA) and LG Chem Co. (Korea) and used without purification.

NP (Nonylphenol)–free reactive nonionic/anionic emulsifiers with excellent physical properties were used to synthesize waterborne acrylic PSAs, while minimizing other factors. Various kinds of PSAs were synthesized to obtain the optimal PSAs, by formulating BA and 2-EHA as main monomers independently or together, and by changing the composition of cohesive monomers, 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. 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 as an initiator in beaker,

Table 1. Monomers 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
Styrene	ST	$CH_2{=}CHC_6H_5$	100
Acrylonitrile	AN	$CH_2{=}CHCN$	105
Methyl methacrylate	MMA	$CH_2{=}C(CH_3)COOCH_3$	105
Vinyl acetate	VAc	$CH_2{=}CHOCOOCH_3$	32
Acrylamide	AAM	$CH_2{=}CHCONH_2$	165
Acrylic acid	AAc	$CH_2{=}CHCOOH$	106

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 to obtain polymer solution with a solid content of 56% and weight average molecular weight of 350,000 g/mol based on GPC analysis.

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 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].

$$1/\mathrm{Tg} = \mathrm{W}_1/\mathrm{Tg}_1 + \mathrm{W}_2/\mathrm{Tg}_2 + \ldots\ldots\ldots\ldots + \mathrm{W}_\mathrm{i}/\mathrm{Tg}_\mathrm{i}$$

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.

Measurements

^{1}H NMR spectrum was recorded on a Bruker Avance NMR spectrophotometer operating at 300 MHz in the Fourier transform mode with $CDCl_3$ as a solvent at a concentration of 2∼3 mg/mL and tetramethylsilane (TMS) as an internal standard. 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 Du Pont 910 thermal analyzer with a heating rate of 10ºC/min in nitrogen atmosphere ranging from −80 to 20°C. The thermal decomposition temperatures (Td) were determined with TGA (Q500, TA Instruments, New Castle, USA) by scanning the samples from 100 to 920°C at a scanning rate of 20°C min^{-1} under nitrogen gas.

Polyethylene terephthalate (PET) film and SUS304 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 100ºC 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 after the 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 1) of acrylic PSAs based on 2-EHA and BA as main monomers with different functional monomers such as VAc, AN, MMA, ST, and AAm 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).

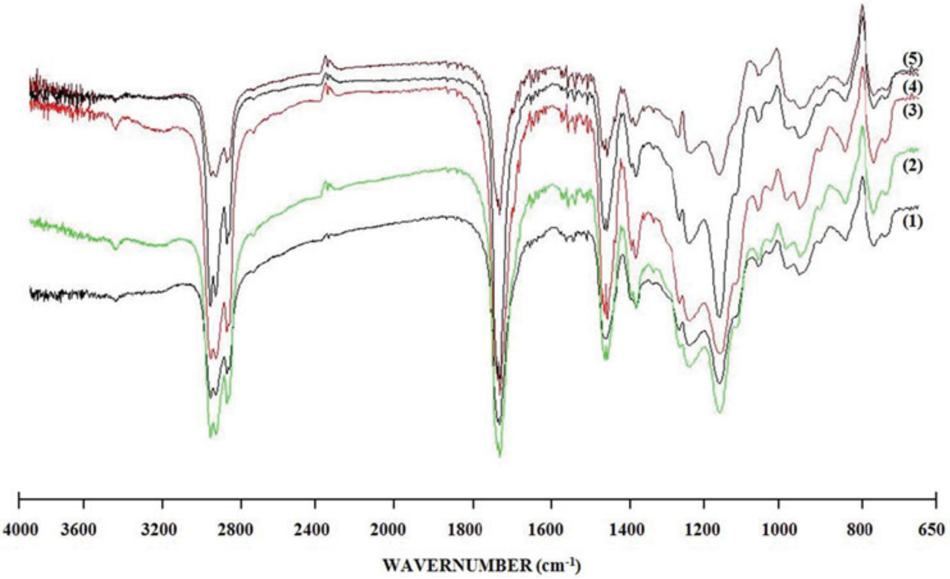

Figure 1. FT-IR spectra of PSAs with different cohesive monomers; (1) VAc, (2) AN, (3) MMA, (4) ST, (5) AAm.

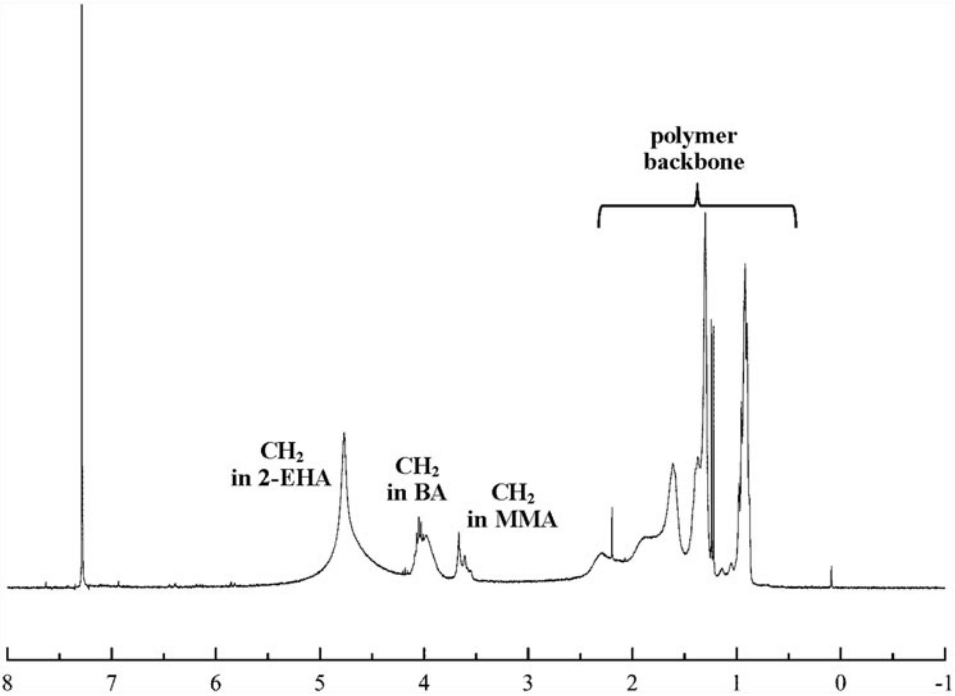

Figure 2. ^{1}H NMR spectrum of PSA based on MC-2.

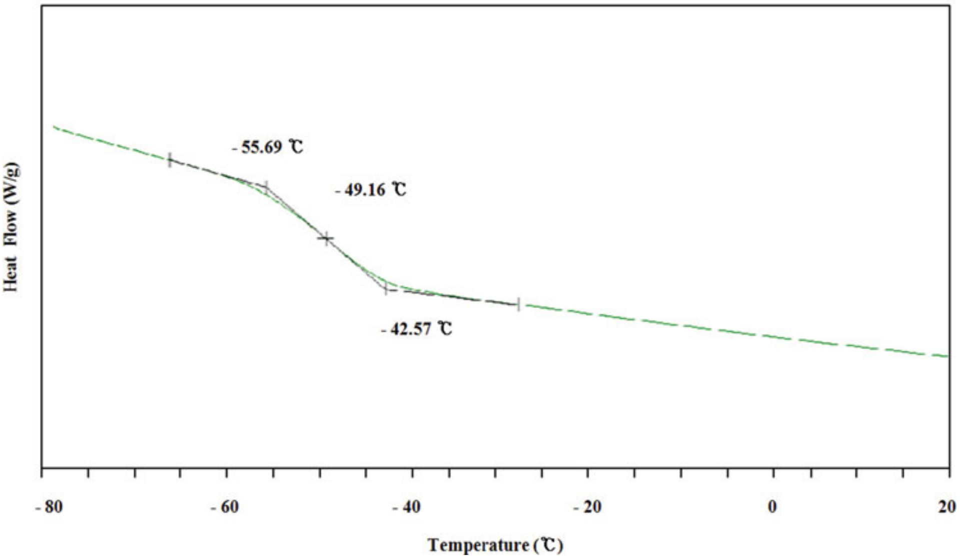

Figure 3. DSC thermogram of acrylic PSA.

As shown in Figure 2, ^{1}H NMR spectrum of PSA (MC-2) showed signals of methylene protons at 4.7, 4.0, 3.6 ppm arisen from EHA, BA, MMA moieties, and polymer backbone at 0.5∼2 ppm with the concurrent disappearance of signals of vinyl protons in monomer moiety at 5.5 and 6.5 ppm.

^{1}H NMR analysis also indicated that the composition of PSA (MC-2) was similar to its formulation in feed based on their integrals of methylene peaks adjacent to ester group shown in Table 5.

DSC permits the determination of glass transition temperature (Tg) of acrylic PSA synthesized from the optimal formulation, 2-ethylhexyl acrylate (2-EHA) and butyl acrylate (BA) as main monomers, and 10 wt% of methyl methacrylate (MMA) as a cohesive monomer. It is commonly accepted that PSAs with lower Tg decrease the light leakage of LCD panel [16]. As shown in Figure 3, the Tg of the PSA was proved to be −49°C, which is relatively good agreement with its theoretical value (−53°C) from Fox equation. Similar findings were also conveyed in the study by Choi et al, who have evaluated the effect of glass transition temperature of PSA on light leakage in LCD panel and indicated that PSA with higher Tg had poorer resistant for film shrinkage as well as higher light leakage [17]. Some deviations between the glass transition temperature determined by DSC and theoretical Tg were found, which may be due to the differences of composition from its formulation as well as the 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 monomer compositions were used to obtain the optimal PSA for LCD devices. First, the acrylic PSAs with solid content of 56% and theoretical Tg of −41°C based on BA as a main monomer, AAc as a functional monomer for bonding strength, were synthesized with different cohesive monomers, such as VAc, AN, MMA, ST, and AAm, and evaluated their peel strengths, such as initial, moisture and heat resistances. The acrylic PSA with VAc as a cohesive monomer (BA-1), as shown in

Table 2. Formulation and physical properties of acrylic PSAs based on BA as a main monomer

Formulations (g)	BA-1	BA-2	BA-3	BA-4	BA-5
BA	88	91	91	91	92
AAc	2	2	2	2	2
VAc	10	—	—	—	—
AN	—	7	—	—	—
MMA	—	—	7	—	—
ST		—	—	7	—
AAm	—	—	—	—	6
Conversion (%)	93	97	100	99	98
Initial peel strength (kgf/25 mm)	0.4	0.7	1	0.9	0.6
Moisture resistant peel strength (kgf/25 mm)	0.4	0.7	0.9	1	0.8
Heat resistant peel strength (kgf/25 mm)	0.7	0.9	1.2	1	0.8

Reaction Conditions : initiator (KPS), 0.3 g; surfactant, nonionic and anionic surfactants were used equivalently; $NaHCO_3$, 0.2g; H_2O, 80 g; theoretical solid content, 56%; theoretical Tg, −41°C; reaction temp., 85°C; reaction time, 8 h.

Table 2, showed the lowest conversion, initial, moisture and heat resistant peel strengths. The PSA with AN (BA-2) showed relatively low conversion and elastic property, that with ST (BA-4) showed low cohesion, and that with AAm (BA-5) showed low initial tack property due to too high cohesive property leading to low initial peel strength. When MMA was used as a cohesive monomer, the synthesized PSA (BA-3) had higher conversion, initial, moisture/heat resistant peel strengths. However, overall, the PSAs synthesized based on BA as a main monomer with Tg of −41°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 2-EHA as a main monomer, AAc as a functional monomer for bonding strength, were synthesized with different cohesive monomers 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 2-EHA had generally higher physical properties compared to those based on BA in Table 2. Among them, PSA with MMA as a cohesive monomer had the highest initial, moisture/heat resistant peel strengths, which are similar results to that based on BA.

In order to obtain the best formulations for PSA for LCD devices, the acrylic PSAs with solid content of 56% and theoretical Tg of -54°C based on both BA and 2-EHA as main monomers, AAc as a functional monomer for bonding strength, were also synthesized with different cohesive monomers, such as VAc, AN, MMA, ST, and AAm, and evaluated their physical properties in similar way to those mentioned above. Table 4 summarized monomer compositions, polymerization conditions, and physical properties for the synthesized PSAs based on two main monomers. In this study, we used initial and moisture/heat resistant peel strengths to evaluate the physical properties of PSAs formulated with different monomer 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 MMA for further formulations because the PSA formulated with

Table 3. Formulation and physical properties of acrylic PSAs based on 2-EHA as a main monomer

Formulations (g)	EH-1	EH-2	EH-3	EH-4
2-EHA	79	85	85	85
AAc	2	2	2	2
VAc	19	—	—	—
AN	—	13	—	—
MMA	—	—	13	—
ST	—	—	—	13
Conversion (%)	93	96	100	99
Initial peel strength (kgf/25 mm)	0.8	1	1.2	1
Moisture resistant peel strength (kgf/25 mm)	0.8	1.1	1.2	1
Heat resistant peel strength (kgf/25 mm)	1	1.2	1.3	1.1

Reaction Conditions : initiator (KPS), 0.3 g; surfactant, nonionic and anionic surfactants were used equivalently; $NaHCO_3$, 0.2g; H_2O, 80 g; theoretical solid content, 56%; theoretical Tg, -54°C; reaction temp., 85°C; reaction time, 8 h.

MMA as a cohesive monomer exhibited the highest and most balanced physical properties among them, which may be more attractive to LCD devices.

In order to evaluate the effect of MMA content as a cohesive monomer 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 AAc as a bonding monomer. As seen in Table 5, at MMA content of 10 wt%, the synthesized PSA had the highest and most balanced initial, moisture and heat resistant peel strengths, meaning that the waterborne acrylic PSA with BA and 2-EHA as main monomers, 10 wt% of MMA as a cohesive monomer, had the optimal physical

Table 4. Formulation and physical properties of acrylic PSAs based on both BA and 2-EHA as main monomers

Formulations (g)	EB-1	EB-2	EB-3	EB-4	EB-5
2-EHA	65	68	68	68	70
BA	20	21	21	21	20
AAc	2	2	2	2	2
VAc	13	—	—	—	—
AN	—	9	—	—	—
MMA	—	—	9	—	—
ST	—	—	—	9	—
AAm	—	—	—	—	8
Conversion (%)	95	96	100	100	100
Initial peel strength (kgf/25 mm)	0.9	1	1.3	1	0.9
Moisture resistant peel strength (kgf/25 mm)	1	1	1.3	1	0.9
Heat resistant peel strength (kgf/25 mm)	1.2	1.2	1.4	1.2	1

Reaction Conditions : initiator (KPS), 0.3 g; surfactant, nonionic and anionic surfactants were used equivalently; $NaHCO_3$, 0.2g; H_2O, 80 g; theoretical solid content, 56%; theoretical Tg, -54°C; reaction temp., 85°C; reaction time, 8 h.

Table 5. Formulation and physical properties of acrylic PSAs; Effect of MMA content

Formulations (g)	MC-1	MC-2	MC-3	Conventional PSA[a]
2-EHA	72	67(64)[b]	62	67
BA	21	21(27)[b]	21	21
AAc	2	2(2)[b]	2	2
MMA	5	10(7)[b]	15	10
Theoretical Tg (°C)	−59	−53	−48	−53
Conversion (%)	100	100	100	100
Mw (× 10^3)	350	350	350	350
Initial peel strength (kgf/25 mm)	1.4	1.3	0.9	1.1
Moisture resistant peel strength (kgf/25 mm)	1.2	1.3	1	1.0
Heat resistant peel strength (kgf/25 mm)	1.2	1.4	1	1.0

Reaction Conditions : initiator (KPS), 0.3 g; surfactant, nonionic and anionic surfactants were used equivalently; $NaHCO_3$, 0.2g; H_2O, 80 g; theoretical solid content, 56%; reaction temp., 85°C; reaction time, 8 h. [a]With conventional non-reactive emulsifier. [b]Resulting contents in parentheses calculated from ^{1}H NMR spectroscopy.

properties. However, as evidence from Figure 4, the PSAs based on 2-EHA, BA, MMA had similar decomposition temperature regardless of their compositions.

Additionally, it was further compared to its conventional PSA synthesized with conventional non-reactive emulsifier. Theoretically speaking, the remained low molecular weight emulsifier in PSA resulted in the decrease in its physical properties, i.e., the less emulsifier

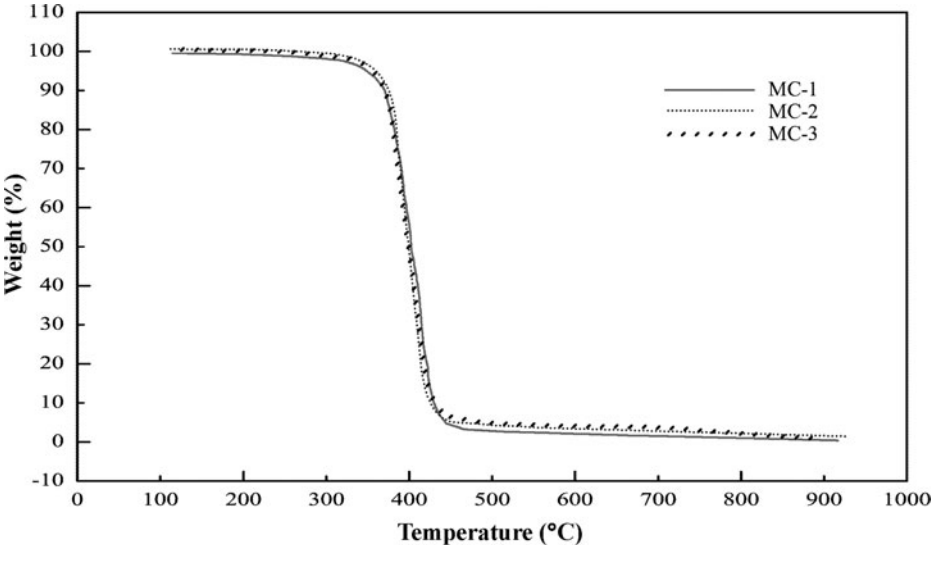

Figure 4. TGA thermograms of PSAs based on 2-EHA, BA, and MMA.

in PSA, the better its physical properties. Although both PSAs had the same compositions and complete conversion to polymers in Table 5, the PSA from reactive emulsifier (MC-2) had higher physical properties in all aspects. This phenomenon may be attributed to the minimized quantities of residual emulsifier, meaning that most reactive emulsifiers were incorporated into polymer chains in PSA.

Conclusions

Various kinds of PSAs with different main and cohesive monomers were applied for the potential use as adhesives between LCD panel and optical films. Among them, PSA based on both BA and 2-EHA as main monomers, 10 wt% of MMA as a cohesive monomer 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 and the evaluation of environmental friendly properties, as well as the synthesis of conductive PSA for LCD devices. Future research will focus on the optical properties, light leakages as well as rheological properties of PSAs depending on their compositions.

Acknowledgments

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References

[1] Son, H. C., Kim, H. G., Lee, D. H., & Min, K. E. (2008). *Polymer (Korea)*, *32*, 313.

[2] Satas, D. (1989). *Handbook of Pressure Sensitive Adhesive Technology, 2nd edition*, Van Nostrand Reinhold: New York.

[3] Benedek, Istvan (2004). *Pressure Sensitive Adhesive and Applications, 2nd edition*, Marcel Dekker: New York.

[4] Pizzi, A., & Mittal, K. L. (2003). *Adhesive Technology and Application*, Marcel Dekker: New York.

[5] Kinloch, A. J. (1986). *Adhesion and Adhesives, Science and Technology, Lausanne*.

[6] Czech, Z. (2001). *J. Appl. Polym. Sci.*, *81*, 3212.

[7] Nam, I. (2011). *J. Adhesion and Adhesives*, *31*, 708.

[8] Gower, M. D., & Shanks, R. A. (2004). *J. Appl. Polym. Sci.*, *93*, 2909.

[9] Asahara, J., Takemura, A., Hori, N., Ono, H., & Matsui, H. (2004). *Polymer*, *45*, 4917.

[10] Chun, H. A., Kim, H. A., Kim, G. S., Kim, J. I., & Lim, K. Y. (2007). *J. Appl. Polym. Sci.*, *106*, 2746.

[11] Sohn, S. M. (2003). *J. Adh. Sci. Tech.*, *17*, 889.

[12] Yang, M. S., Ko, S. W., & Choi, H. J. (2009). *J. Macro. Sci. Part A : Pure Appl. Chem.*, *46*, 1142.

[13] Sperling, L. H. (2001). *Intro Phys. Polym. Sci.*, 342.

[14] Zhang, G., Zhang, J., Wang, S., & Shen, D. (2003). *J. Polym. Sci.: Part B: Polym. Phys.*, *41*, 23.

[15] Jeong, B.Y., Chun, J.H., Cheon, J.M., & Park, G.H. (2012). *J. Adhesion and Interface* (Korea), *13*, 89.

[16] Chem, Dong Woo Fine (2008). *Korea, Technical Report*.

[17] Yang, M. S., Ko, S. W., & Choi, H. J. (2009). *J. Macromol. Sci. Part A: Pure and Appl. Chem.*, *46*, 1142.