Electronic Supplementary Information

Ambient air-operated thermo-switchable adhesion of *N*-isopropylacrylamide incorporated pressure sensitive adhesives

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Supplementary Notes

Materials

2-Ethylhexyl acrylate (EHA) (\geq 98%), acrylic acid (AA) (\geq 99%), and *N*-isopropylacrylamide (NIPAM) (\geq 99%) were purchased from Sigma-Aldrich. Hydrophobic fumed silica (Aerosil R 974) was purchased from Evonik Industries. 1,6-Hexanediol diacrylate (HDDA) was purchased from Alfa Aesar. Phenylbis (2,4,6-trimethyl-benzoyl) phosphine oxide was purchased from TCI Chemicals. The polyethylene terephthalate (PET) film (SH82) and releasing film (SG31) were purchased from SKC. A heating plate (PTC heating element, 24 V, and 80 °C) was purchased from LJXH.

Synthesis of NIPAM-incorporated PSAs

Acrylate-based PSAs were synthesized by random copolymerization of three different acrylic monomers: EHA, AA, and NIPAM. Table S1 lists the composition molar ratio of each acrylate monomer. A crosslinking agent (HDDA, 0.15 mol%) was added to the mixture of acrylic monomers, followed by the addition of hydrophobic fumed silica (~ 10 phr) as an inorganic filler to control the viscosity of the mixture. After adding a photoinitiator (phenylbis (2,4,6-trimethyl-benzoyl) phosphine oxide, 0.1 mol%), the mixture was blended using a vortex mixer (~3 min). Then, the mixture was coated between a PET film and a releasing film using a knife-coating device (KP-3000VH, KIPAE, South Korea). The coated layer was cured for 5 min at a distance of 5 cm under a UV lamp (100 W, 365 nm). The final thickness of the synthesized PSAs was ~100 μm.

Characterization of synthesized PSAs

A 600 MHz NMR spectrometer (VNMRS, Agilent, USA) was used in a solid state to obtain proton nuclear magnetic resonance (1H NMR) spectra. Fourier-transform infrared (FTIR) spectra were obtained using a FT–IR spectrometer (FT/IR-4600, JASCO, Japan) by transmittance mode. In the case of molecular weight measurement, the linear polymers without crosslinker were synthesized by using methyl acrylate instead of acrylic acid to avoid inaccurate results due to acrylic acid.¹ The molecular weight of linear polymers was measured using gel permeation chromatography (GPC, 1200S, Agilent, USA) after dilution in tetrahydrofuran (THF) and filtration through a 0.2 µm filter. Tensile strength was measured using a universal testing machine (WL2100C, Withlab, South Korea) at a crosshead speed of 100 mm/min at room temperature. The glass transition temperature was measured using differential scanning calorimetry (DSC, Q200, TA Instrument, USA) at a scanning rate of 10 °C/min under a nitrogen atmosphere from -60 to 120 °C. Thermogravimetric analysis (TGA, Q400, TA Instruments, USA) was used to evaluate thermal stability. The weight loss of the specimen was monitored at a heating rate of 10 °C/min in a nitrogen atmosphere from 40 to 600 °C. Rheological properties were measured using a rheometer (Kinexus pro+, NETZSCH, Germany), in which the frequency sweep mode ranged from 0.1 to 100 Hz with 0.025% strain at various temperatures (20, 25, 40, 60, and 80 °C). Morphology and energy dispersive X-ray spectroscopy (EDS) were performed using a scanning electron microscope (SEM, SU8220, Hitachi High-Technologies, Japan). The transmittance of the PSA films was measured by UV-Vis-NIR spectroscopy (V-750, JASCO, Japan). The PSA films were attached to the glass substrate, and the transmittance at 650 nm was used as a reference. The transmittance of the PSA was scanned in the wavelength range from 250-650 nm.

Peel adhesion test

PSA films ($25 \times 200 \text{ mm}$) were attached to various substrates (stainless steel (SUS304), PET, glass, Polypropylene (PP), high density polyethylene (HDPE), and Teflon) by pressing a 2.5 kg hand-roller twice at a speed of 10 mm/s, and then contacted at room temperature for 15 min before the peel adhesion test. A universal testing machine (WL2100C, Withlab, South Korea) was used to evaluate the peel strength of the PSAs at room temperature with a crosshead speed of 300 mm/min. The peel strength was defined using the ASTM D3330 method with a unit of N/25mm. To elucidate the temperature dependency of the peel strength, the PSA film was attached at room temperature followed by thermal annealing at 80 °C for 5 min and equilibrating at different temperatures (0, 20, 40, 60, 80, 100, and 120 °C) for 10 min, which resulted in a total contact time of 15 min. Temperature-dependent peel adhesion tests were performed at a crosshead speed of 300 mm/min using a temperature-controllable universal testing machine (QM100T, QMESYS, South Korea).

Surface energy measurement

Surface energy was calculated based on the Fowkes theory.²⁻³ The polar and dispersive components of the PSA film surface energy were analyzed using DI water and diiodomethane contact angle analysis. The surface tension values at each temperature were used to calculate the surface energy at each temperature.⁴ The PSA film was attached to the SUS substrate for 15 min in a convection oven at a specific temperature (room temperature or 80 °C) prior to the contact angle measurement. The contact angles of the droplets on the detached PSA films were measured using a drop shape analyzer (DSA100S, Kruss Gmbh, Germany). The heating plate was deposited under the PET films for temperature maintenance during the contact angle measurements.

Residual analysis

The PSA film was attached to the SUS substrate by pressing a 2.5 kg hand-roller twice at a speed of 10 mm/s, and then sequentially contacted at room temperature (~25 °C) and 60 °C for 10 min and 5 min, respectively. After heating, we immediately detached the PSA film from the SUS substrate. For room temperature (~25 °C) peeling samples, all procedures are conducted at room temperature. After peeling, the SUS substrates were analyzed by SEM EDS mode.

Removable property evaluation

The temperature-responsive removability of PSA film was evaluated by recording the detachment time of the SUS304 substrate during heating, and according to the weight (100,

200, 300, and 500 g). Each PSA film adhered to the SUS304 substrate for 15 min, and then the weight was fixed at the end of the PSA film. After the equilibrium time (> 1 min), the heating plate was placed on the SUS304 substrate, and the time until the PSA film detached from the SUS304 substrate was recorded.

Reversible adhesion test

The probe tack test was performed using a texture analyzer (TXA, Yeonjin, South Korea). The probe tack test was performed by approaching the PSAs with a 5 mm cylindrical probe (stainless steel) at a speed of 10 mm/s, followed by a 1 s bonding time on PSAs at a load of 1 N. The probe was separated from the PSAs at a speed of 10 mm/s. The temperature of the probe tack test was also controlled using a heating plate, and heating and cooling cycles were repeated to analyze the thermo-switchable adhesion properties.



Figure S1. ¹H NMR spectra of the synthesized PSAs films. (a) $E_8A_2N_0$, (b) $E_8A_1N_1$ and (c) $E_8A_0N_2$.



Figure S2. Fourier transform infrared (FT-IR) spectra of the synthesized PSA films.



Figure S3. Gel permeation chromatography (GPC) trace of linear copolymers of the $E_8A^*_2N_0$, $E_8A^*_1N_1$ and $E_8A^*_0N_2$ (A^* indicates copolymer synthesized by methyl acrylate instead of acrylic acid).



Figure S4. Stress-strain curves of the synthesized PSA films.



Figure S5. DSC thermograms of the synthesized (a) PSA films (with crosslinker) and (b) linear polymer (without crosslinker). DSC thermograms showing T_{gs} of E₈A₂N₀, E₈A₁N₁, E₈A₀N₂ with or without crosslinker.



Figure S6. TGA thermograms showing 5% degradation temperature (T_{5d}) of E₈A₂N₀, E₈A₁N₁, E₈A₀N₂.



Figure S7. UV-vis transmittance spectra of the synthesized PSA films.



Figure S8. Rheological properties of the PSA films. (a) Storage modulus and (b) Loss modulus at the room temperature (25 °C) The loss modulus of (c) $E_8A_2N_0$ and (d) $E_8A_0N_2$ at various temperatures (20, 40, 60, and 80 °C).



Figure S9. A quadrant PSA performance window and plots showing the G' and G" value of synthesized PSAs measured at a frequency range of 0.01 - 100 rad/sec.

mol%	$E_{10}A_0N_0$	$E_9A_0N_1$	$E_8A_0N_2$	$E_8A_1N_1$	$E_8A_2N_0$
EHA	100	90	80	80	80
AA	0	0	0	10	20
NIPAM	0	10	20	10	0

Table S1. Composition of synthesized PSAs. Monomer of the synthesized PSAs in terms of mol%. All samples include crosslinker (0.15 mol%) and photoinitiator (0.1 mol%) with respect to total monomer concentration.

	M_n (g/mol) ^a	$M_w (\mathrm{g/mol})^b$	$\boldsymbol{D} (\boldsymbol{M}_{w}/\boldsymbol{M}_{n})^{c}$
E ₈ A [*] ₂ N ₀	121252	348187	2.872
$E_8A_1^*N_1$	128146	356105	2.779
$E_8A_0^*N_2$	122511	446923	3.648

Table S2. Molecular weight of the linear polymers without crosslinker (A^{*} indicates copolymer synthesized by methyl acrylate instead of acrylic acid)

^{*a}</sup><i>M_n*: Number average molecular weight</sup>

 ${}^{b}M_{w}$: weight average molecular weight

^{*c*}*Đ*: Polydispersity index (PDI)

	$E_8A_2N_0$	$E_8A_1N_1$	$E_8A_0N_2$
Young's modulus (kPa)	313 ± 46	209 ± 16	147 ± 22
Toughness (MJ/m ³)	3.01 ± 0.58	2.40 ± 0.27	1.6 ± 0.27
Ultimate tensile strength (MPa)	1.52 ± 0.2	1.44 ± 0.2	0.9 ± 29.7
Elongation at break (%)	480 ± 7.93	518 ± 40.8	499 ± 29.7

Table S3. Mechanical properties of the synthesized PSA films.

		Contact angle (°)		Surface energy (mJ/m ²)		
		Water	Diiodomethane	Dispersive (γ^D)	Polar (γ^{P})	Total (y)
E ₈ A ₂ N ₀	25 °C	77.4 ± 1	46.8 ± 2	36 ± 1	3.9 ± 0.1	40 ± 1.1
	80 °C	$78.4~\pm~0.6$	47.3 ± 1.7	31.3 ± 0.8	4.6 ± 0.01	36 ± 0.8
E8A0N2	25 °C	87.4 ± 0.9	42.8 ± 1.2	38.2 ± 0.6	0.9 ± 0.08	39 ± 0.7
	80 °C	94.3 ± 0.8	50.3 ± 2.6	30 ± 1.3	0.8 ± 0.05	30.7 ± 1.3

Table S4. Contact angle and surface energy of $E_8A_2N_0$ and $E_8A_0N_2$.

Supplementary References

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