Supporting Information
Biomimetic Hot-Melt Adhesive using Galloyl-grafted Polypropylene for Multi-substrates

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Table S1. Physical properties of PP *F-704NP*™.

Melt mass-flow rate at 230 °C (g/10 min)	7.0
Tensile stress at yield (MPa)	32
Nominal tensile strain at break (%)	>200
Modulus if elasticity in tension (MPa)	1,250
Rockwell hardness	95

Preparation and characterization of BAMA and PPBA

BAMA was synthesized first and used as monomer. Benzoic acid (5 g, 1 equiv.) was added to a three-neck flask equipped with a condenser, followed by the addition of glycidyl methacrylate (8.7 g, 1.5 equiv.) and triethylamine (1.11 g, 0.1 equiv.) as a catalyst. The reaction mixture was purged with nitrogen gas for 30 minutes before the addition of dehydrated acetonitrile (80 mL) as the solvent. The flask was then placed in an oil bath and stirred at 80 °C for 8 hours. The reaction scheme is illustrated in Figure S1. After the reaction was complete, the mixture was cooled to room temperature, and the acetonitrile solvent was removed by evaporation. The residue was dissolved in dichloromethane and washed sequentially with 5% potassium carbonate solution and saturated sodium chloride solution. The organic layer was separated, dried, and purified via column chromatography using an ethyl acetate/hexane (1:7, v/v) solvent system. A colorless oily product was obtained and characterized by ^{1}H NMR and FTIR spectroscopy.

The ^{1}H NMR spectra of the synthesized BAMA were confirmed by a JEOL ECS-400 400MHz NMR instrument. Fourier transform infrared spectroscopy (FTIR) was performed on BAMA and PPBA using a JASCO FT-IR 6100 with a KBr pellet. Differential scanning calorimetry (DSC) was conducted using a Shimadzu DSC-60 Plus instrument equipped with a liquid nitrogen cooler, at a

heating and cooling rate of 10 °C min^{-1}. Adhesive polymers were heated from room temperature to 220 °C, cooled to −50 °C, and reheated to 220 °C over two cycles. The heat flow and temperature values were analyzed using data from the second heating cycle.

The successful synthesis of the BAMA monomer was confirmed by ^{1}H NMR spectroscopy, with the corresponding peaks shown in Figure S2a. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10–8.00 (m, 2H), 7.61–7.53 (m, 1H), 7.48–7.40 (m, 2H), 6.16 (s, 1H), 5.62 (s, 1H), 4.50–4.20 (m, 5H), 1.95 (s, 3H). Following polymerization of the BAMA with PP, FTIR measurements were conducted for BAMA, pristine PP, and PPBA. The FTIR spectra are shown in Figure S2b. In the FTIR spectrum of PPBA, a strong carbonyl (C=O) stretching peak at 1716 cm^{-1} was observed—consistent with the peak seen in the BAMA. Additionally, prominent peaks at 2951 cm^{-1} and 2920 cm^{-1} were present, corresponding to the asymmetric stretching vibrations of CH_3 and CH_2 groups, respectively, matching those of pristine PP.

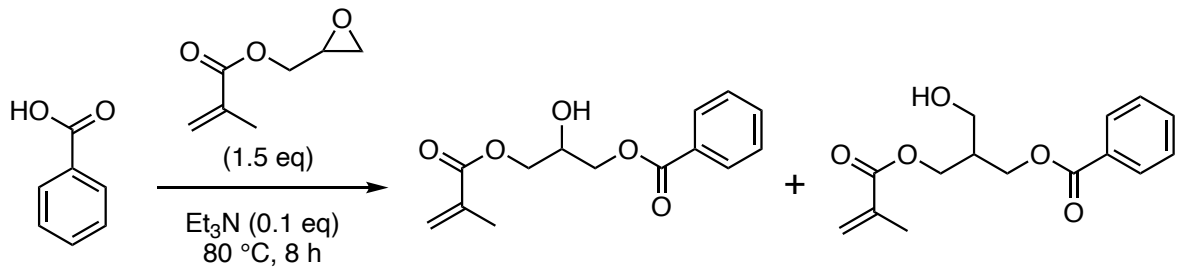

Figure S1. Synthesis route of benzoic-acid-bearing methacrylate monomer (BAMA).

(a) (b)

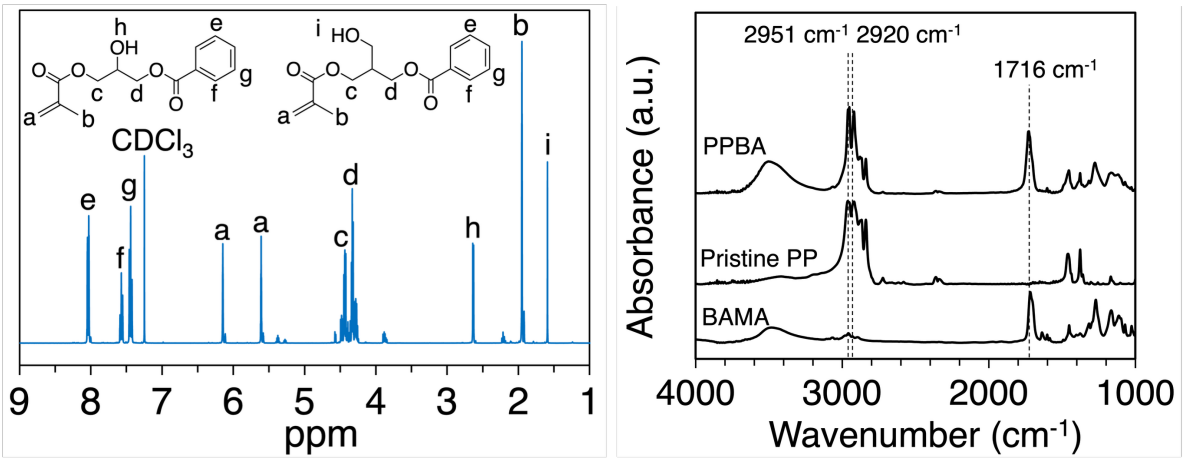

Figure S2. (a) ^{1}H NMR spectra of BAMA using $CDCl_3$ solvent. (b) FTIR spectra of BAMA, pristine PP and PPBA.

Characterization of PPCA

FTIR measurements were conducted on both pristine PP and PPCA. The corresponding FTIR spectra, shown in Figure S3, revealed a new peak at 1700 cm^{-1} in the PPCA spectrum, characteristic of the carbonyl (C=O) stretching vibration. Additionally, prominent peaks at 2951 cm^{-1} and 2920 cm^{-1} were observed, corresponding to the asymmetric stretching vibrations of the CH_3 and CH_2 groups, respectively.

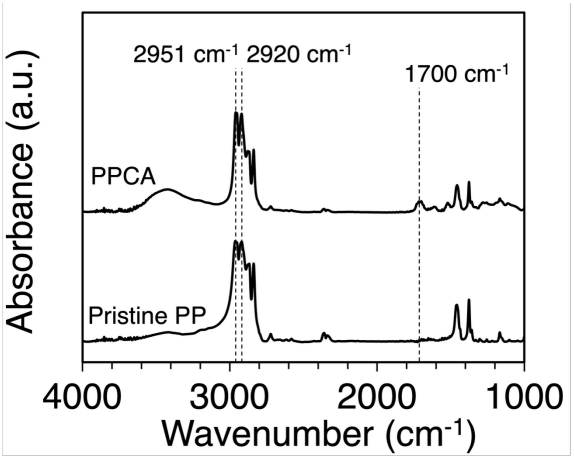

Figure S3. FTIR spectra of pristine PP and PPCA.

Characterization of PPMA

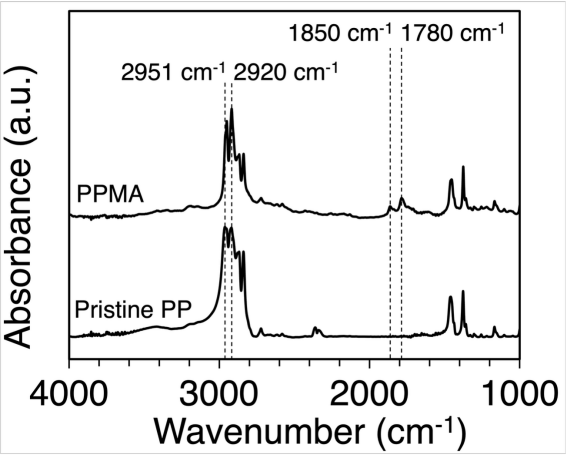

Figure S4. FTIR spectra of pristine PP and PPMA.

FTIR measurements were conducted on both pristine PP and PPMA. The FTIR spectra, presented in Figure S4, show characteristic peaks for PPMA at 1780 cm^{-1} and 1850 cm^{-1}, corresponding to the C=O (carbonyl) stretching vibrations of the cyclic anhydride. Prominent peaks at 2951 cm^{-1} and 2920 cm^{-1} were also observed, attributed to the asymmetric stretching vibrations of CH_3 and CH_2 groups, respectively.

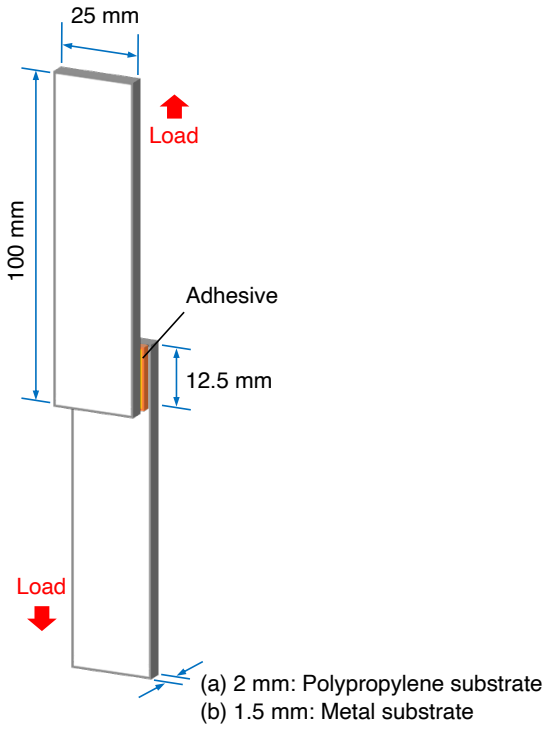

Figure S5. Schematic illustrations of single-lap shear specimen with thickness of 2 mm for PP substrate and 1.5 mm for metal substrates bonded with the hot-melt adhesive.

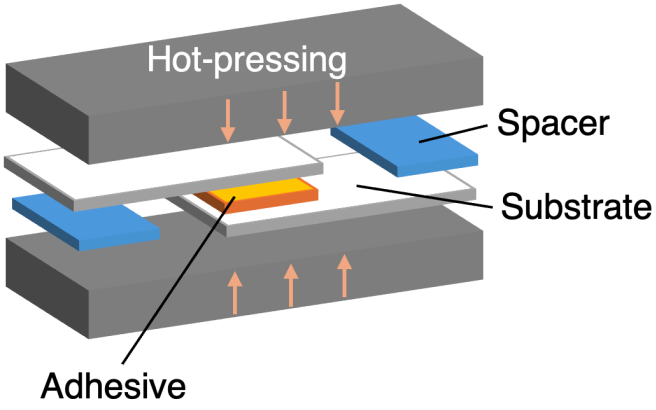

Figure S6. Hot-pressing apparatus used for specimen fabrication.

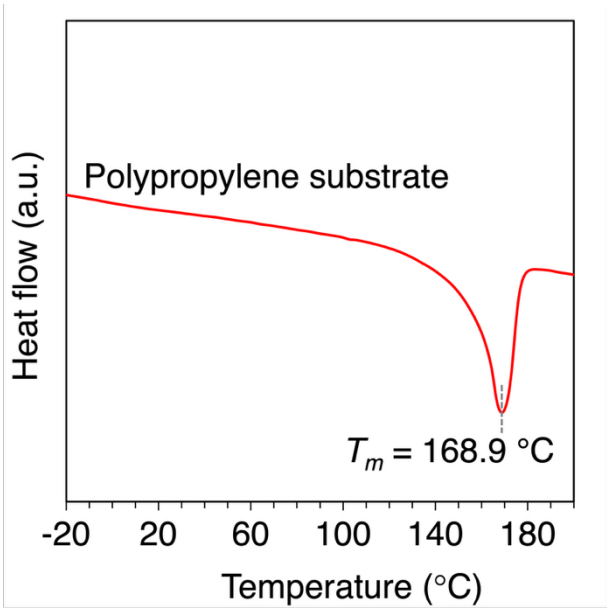

Figure S7. DSC profile of the PP substrate (second heating scan).

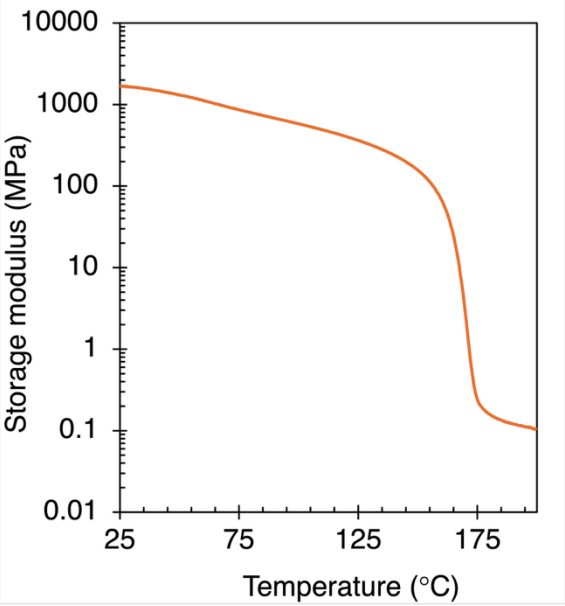

Figure S8. DMA profile of the PP substrate.

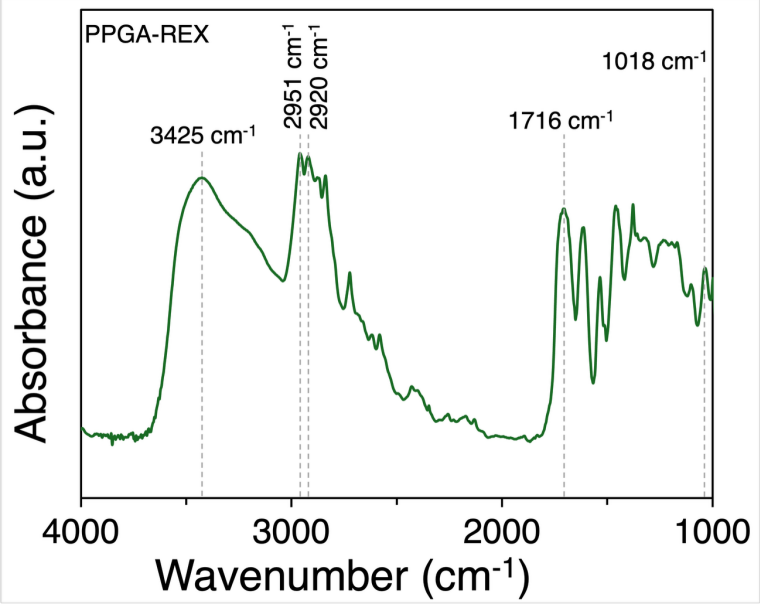

Figure S9. FTIR spectra of PPGA-REX with preparation ratio of 15.9 mol % synthesized from reactive extrusion.

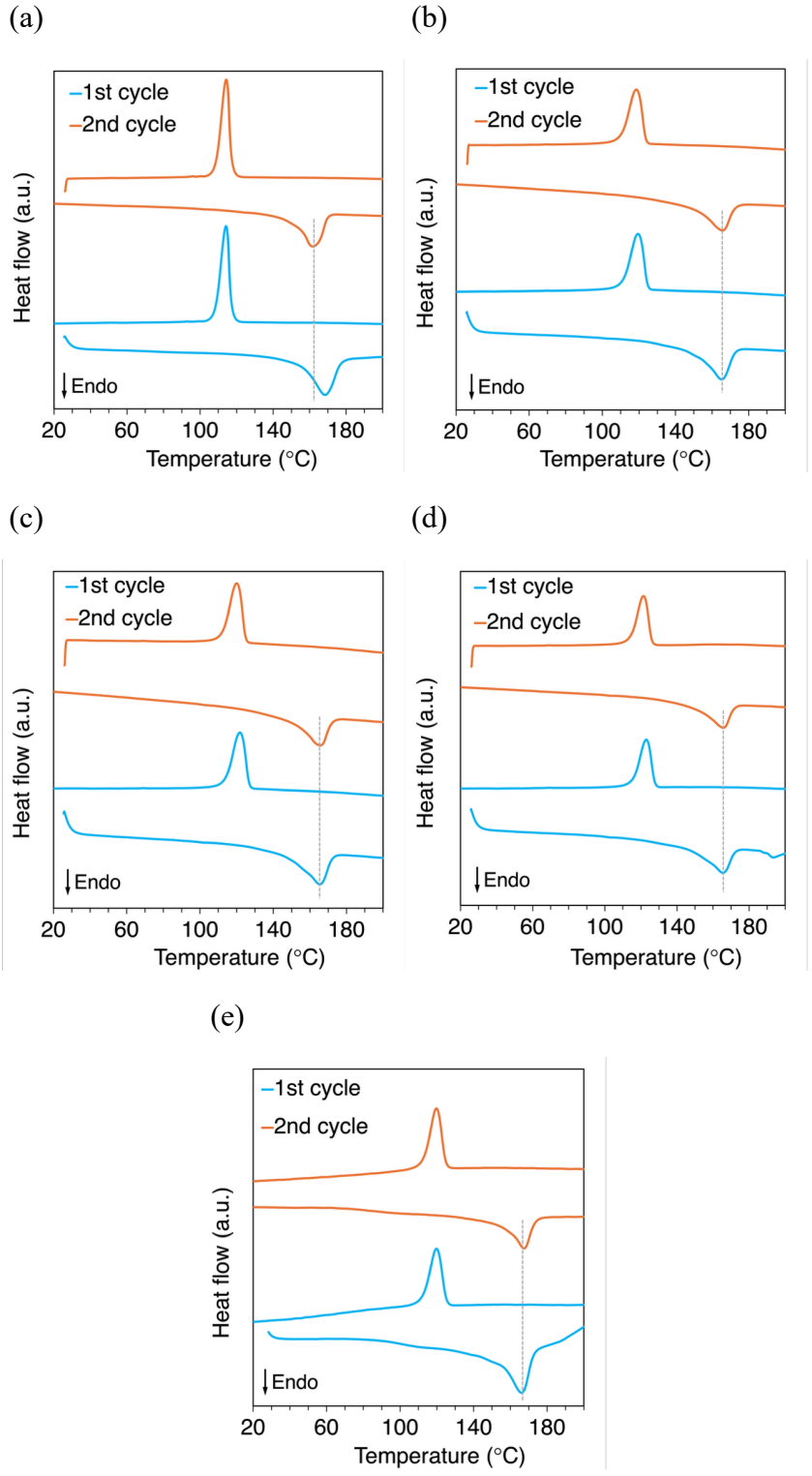

Figure S10. Comparison of the first and second heating scan of DSC profiles of (a) pristine PP, (b) PPGA6.2, (c) PPGA8.9, (d) PPGA10.6 and (e) PPGA11.8 adhesive polymers.

Thermal properties of PPBA, PPCA and PPMA

DSC analysis of the second heating scan revealed the melting temperatures (T_m) of the comparative polymers, as shown in Figure S10. PPBA showed a T_m of 157.2 °C, which is lower than that of pristine PP. PPCA showed a T_m of 163.9 °C, slightly higher than pristine PP. PPMA showed a T_m of 154.0 °C, also lower than pristine PP.

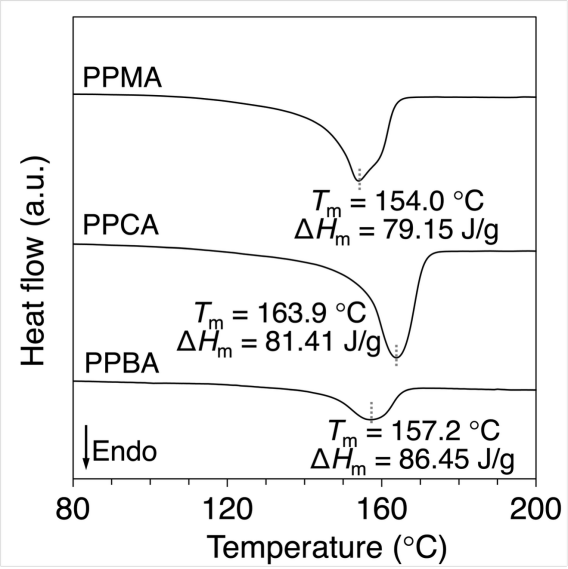

Figure S11. DSC profiles with melting temperature of PPBA, PPCA and PPMA adhesive polymers (second heating scan).

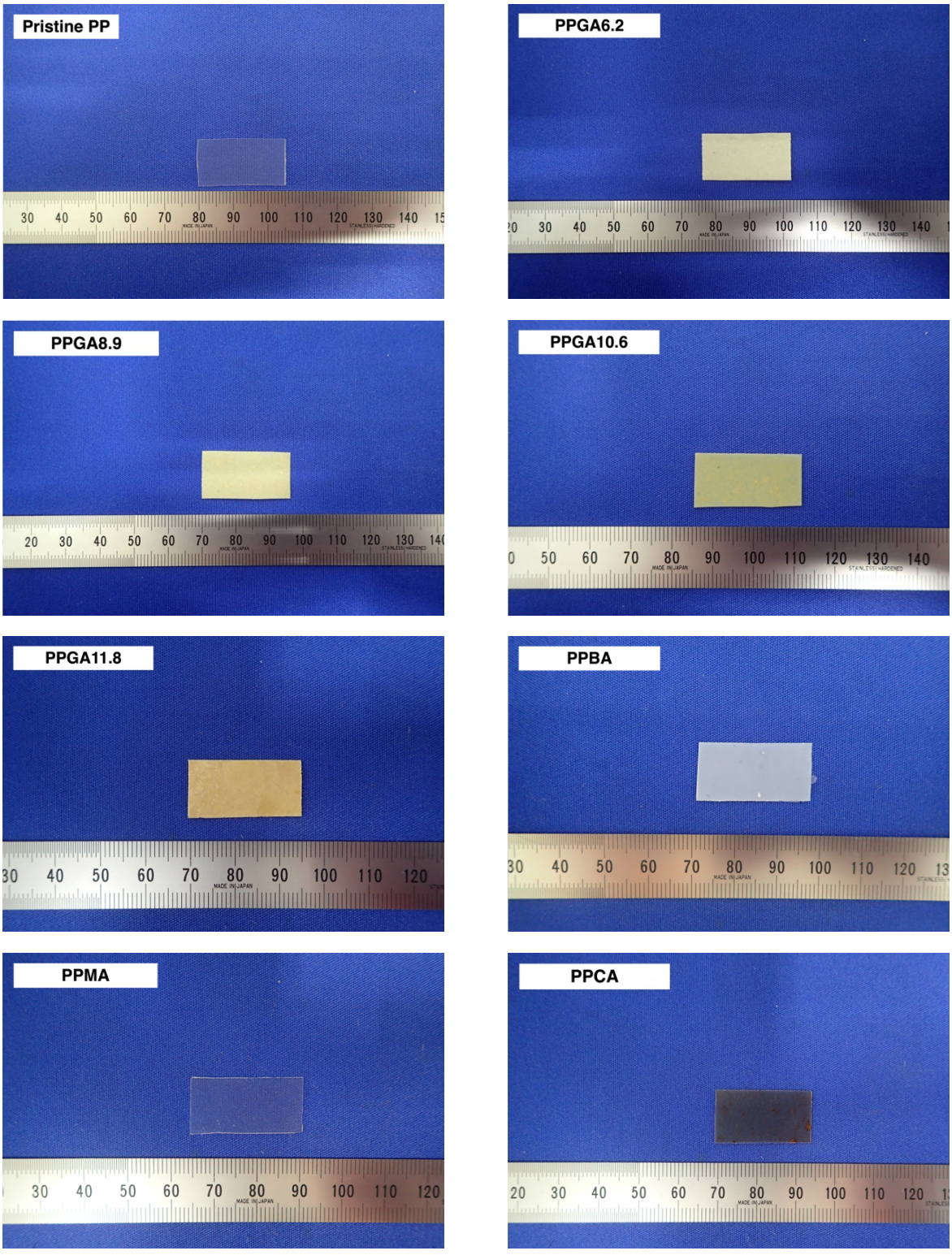

Figure S12. Hot-melt adhesive films after prepared by hot-pressing at temperature of 175 °C and pressure of 10 MPa for 5 min.

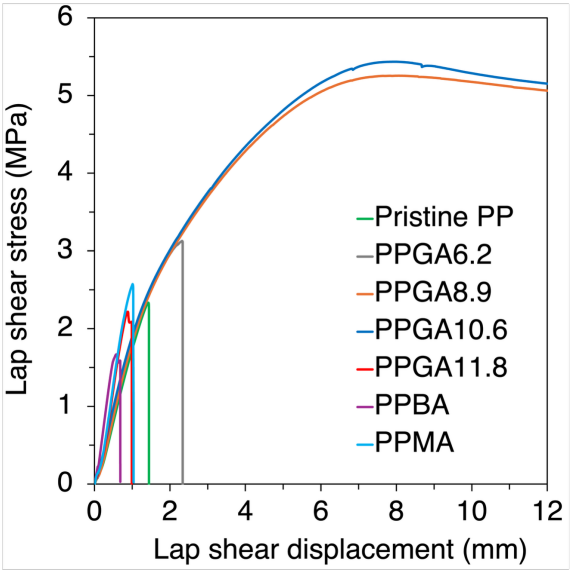

Figure S13. Lap-shear stress and displacement curves of pristine PP, PPGA, PPBA and PPMA adhesives on PP substrate.

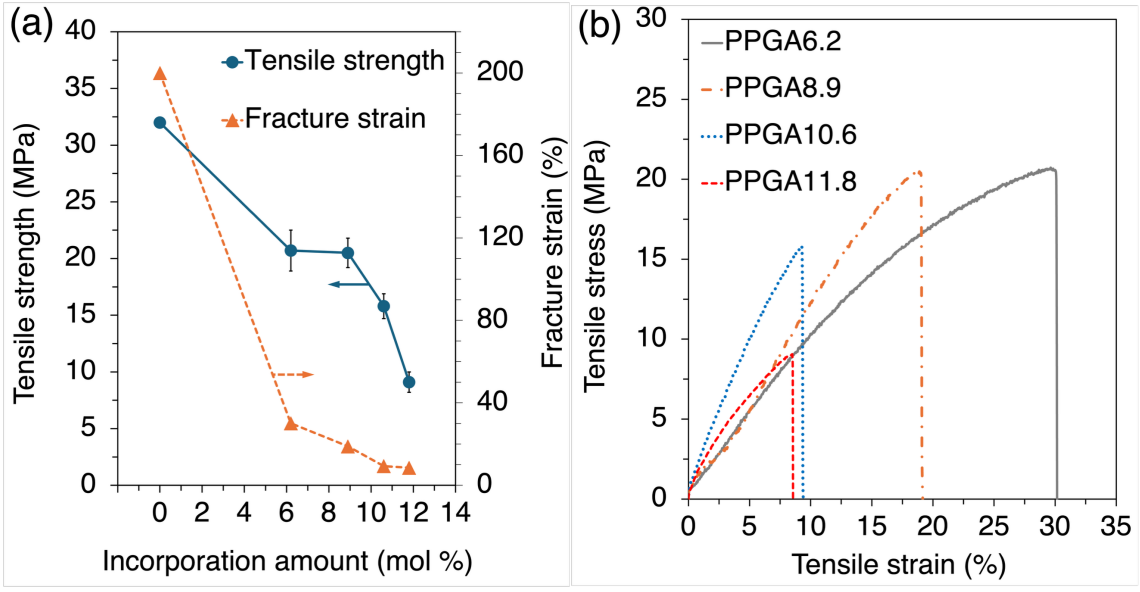

Figure S14. (a) Tensile strength and fracture strain of hot-melt adhesive polymer films plotted as a function of incorporation amount of GAMA. (b) Tensile stress–strain curves of PPGA adhesive films with varying galloyl content.

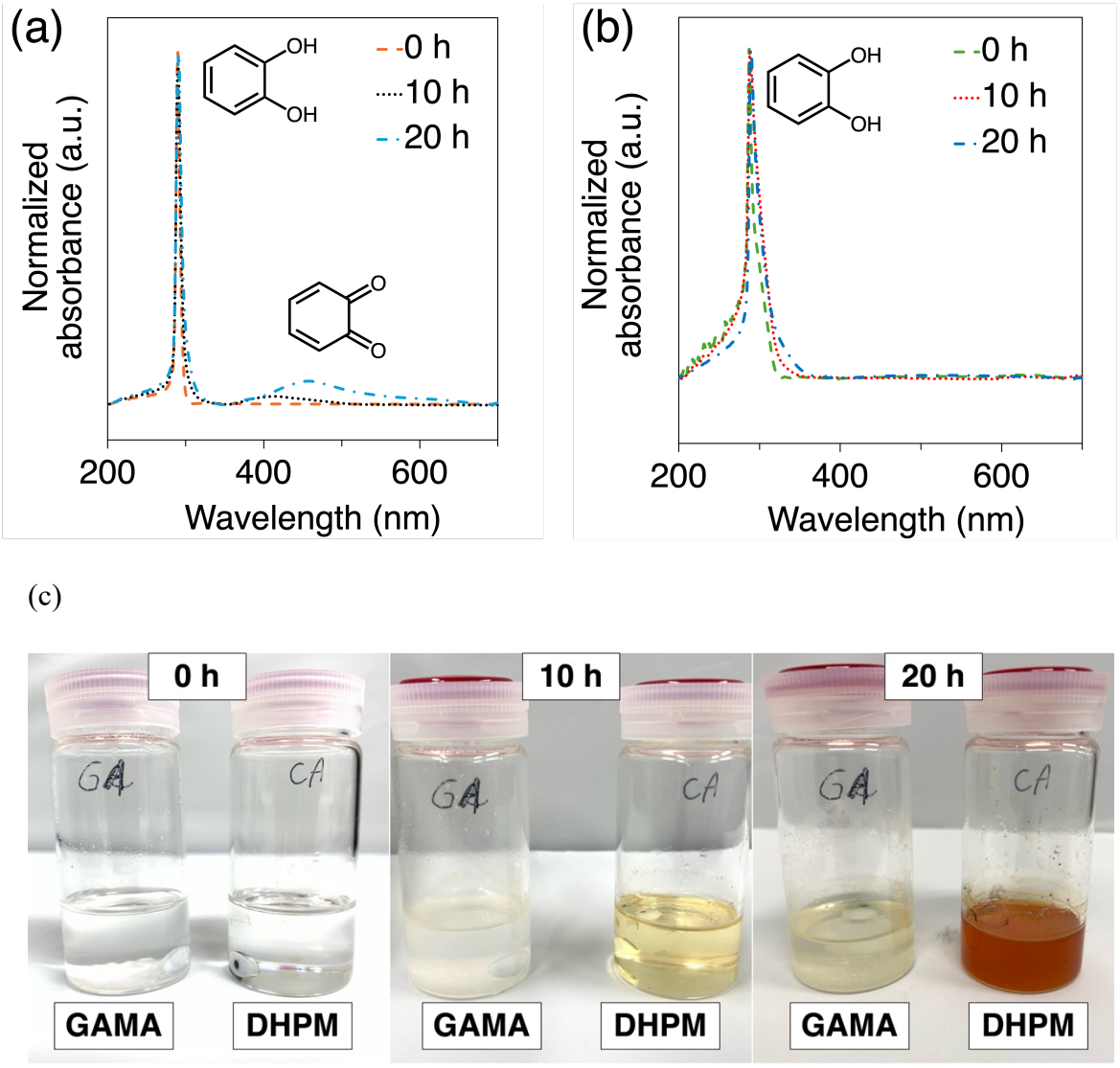

Figure S15. (a) and (b): UV/Vis spectra of DHPM and GAMA, respectively, mixed with dicumyl peroxide and heated at 100 °C for 0 to 20 h. (c) Images showing color change of GAMA (left) and DHPM (right) over 20 h at 100 °C in the presence of dicumyl peroxide.

Surface treatment and characterization of PP and metal substrates

The surfaces of PP substates were cleaned by ultrasonic washing in acetone for 10 minutes, followed by ethanol for another 10 min. After drying, the PP substrates were ready for lap-shear strength adhesion testing. The surfaces of metal substrates, including aluminum alloy, stainless steel, and copper, were first polished with sandpaper and then rinsed with tap water. They were then immersed in a 300 ml beaker containing alkaline degreasing solution consisting of sodium carbonate (4 g), sodium dodecyl sulfate (100 mg), sodium hydroxide (50 mg) and deionized water (200 ml) at 80 °C for 5 minutes. Immediately after removal, the metal substrates were transferred to another beaker containing 300 ml of deionized water to rinse off the solution for a few seconds. The surfaces were then rapidly wiped off the water for a couple times. After drying, the metal substrates were ready to use for lap-shear adhesion testing.

The thermal properties of PP substrates were analyzed using DSC and DMA. The DSC profile from the second heating scan indicated a melting temperature (T_m) of 168.9 °C (Figure S7). Additionally, the DMA profile between 25 and 200 °C showed that the storage modulus of the PP substrate decreased drastically by three orders of magnitude once the temperature exceeded 165 °C (Figure S8). Based on these results, the optimal hot-pressing temperature for fabricating single-lap shear specimens of PP substrate was determined to be 160 °C. This temperature not only prevents deformation of the PP substrates but also facilitates proper bonding between the hot-melt adhesive films and the polymeric substrates. To further assess surface properties, the contact angles of both polymeric and metal substrates were measured using a DMs-401 contact angle meter (Kyowa Interface Science, Japan) and are reported in Figure S16. The PP substrates exhibited a high contact angle, indicating low surface energy. In contrast, the metal substrates displayed lower contact angles, suggesting a higher surface energy.

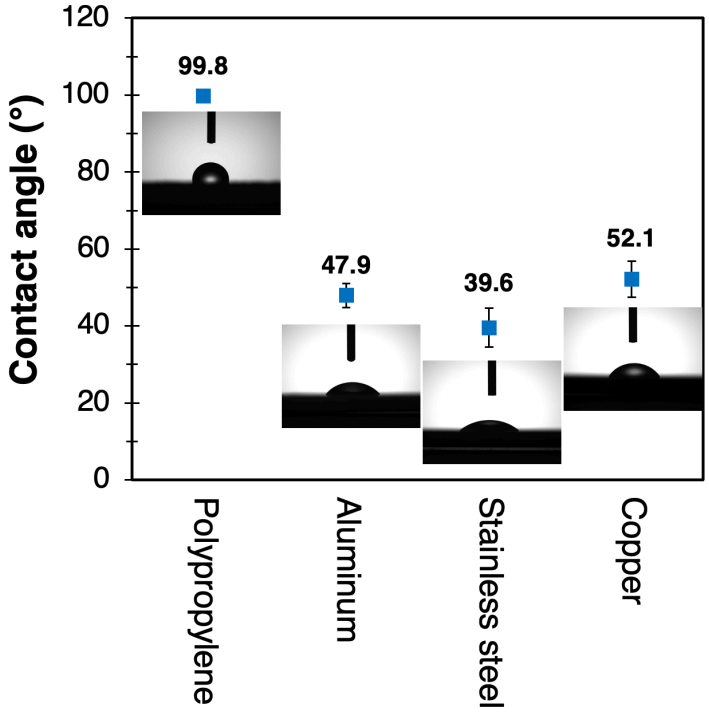

Figure S16. Contact angle measurement of the substrates after surface preparation.

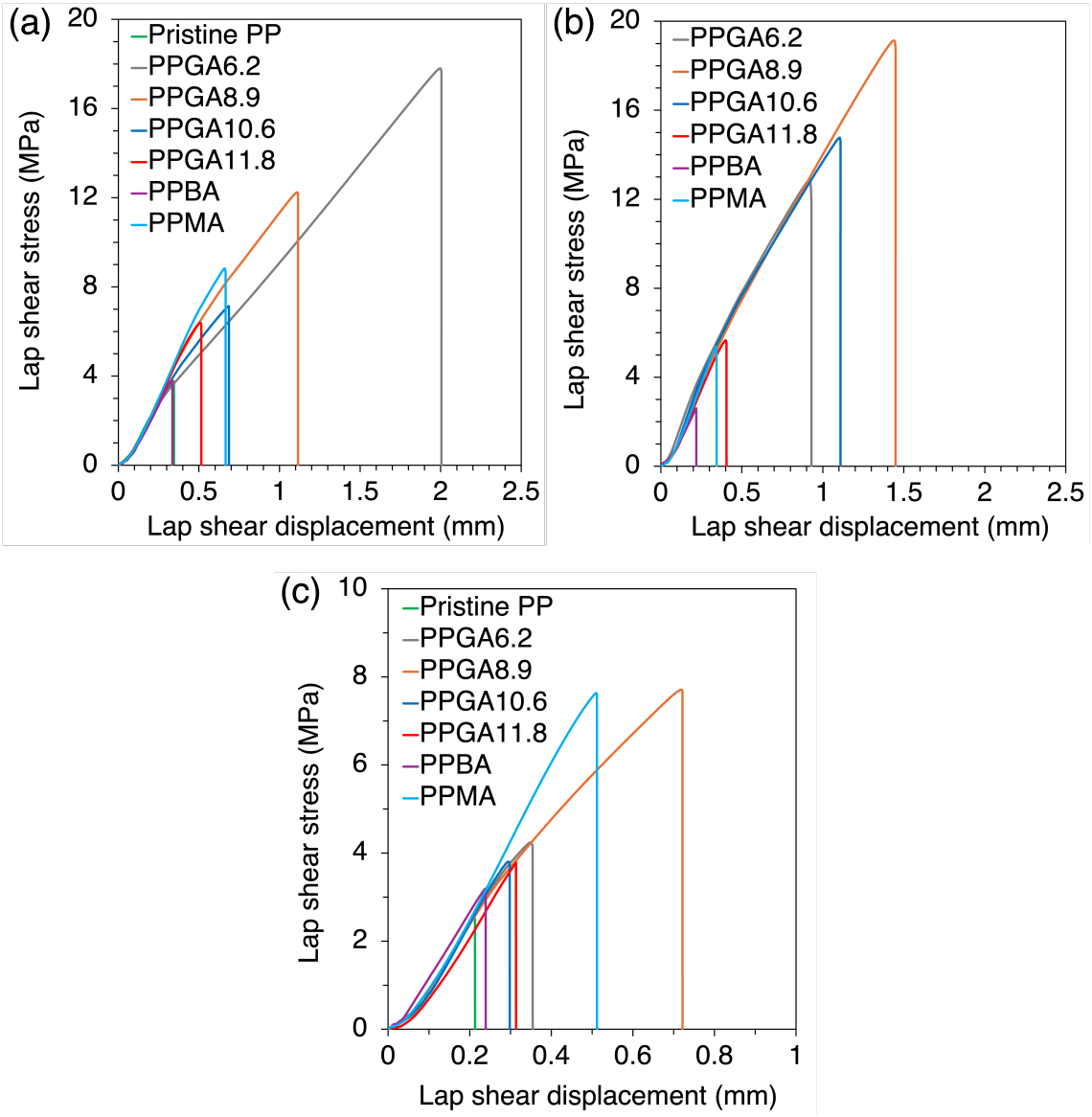

Figure S17. Lap-shear stress-displacement curves on (a) aluminum, (b) stainless steel, and (c) copper substrates.

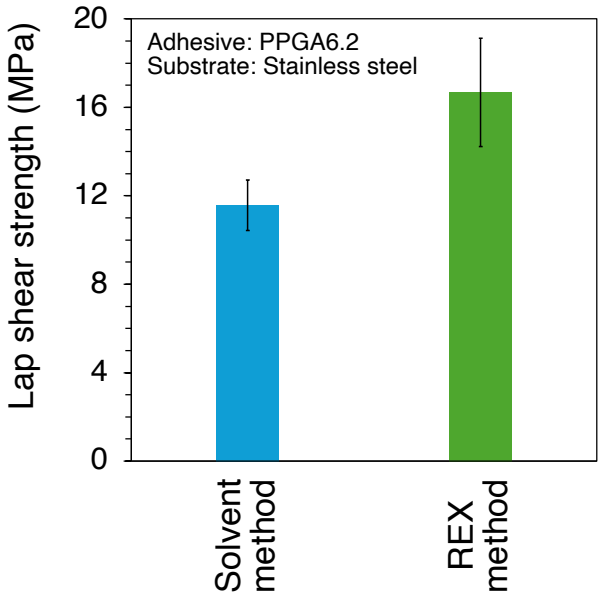

Figure S18. Comparison of lap-shear strength of PPGA6.2 prepared by solvent method and reactive extrusion (REX) method on stainless steel substrates.

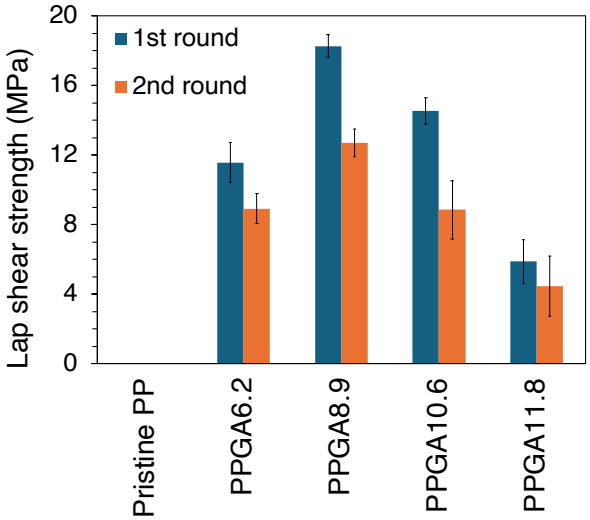

Figure S19. Comparison of the lap-shear strength of pristine PP and PPGA adhesives on stainless steel substrates between the first and second cycles (reusability test).

Table S2. Summary of lap shear strength comparing between this work and previous studies.

Adhesives	Substrates	Bonding method	Lap shear strength (MPa)	References
PPGA8.9	PP	Hot-pressing (160 °C, 0.5 MPa, 3 min)	5.3*	This work
PPGA10.6	PP	Hot-pressing (160 °C, 0.5 MPa, 3 min)	5.4*	This work
Poly(isobornyl acrylate)	PP	Pressing with 1 kg weight, 23 °C, 60 min	0.6	[1]
DOMA-EHMA	PP	Pressing with pair of metal clamps at 70 °C, 60 min	1.3	[2]
3M™ 3731	PP	Hot-melt adhesive (177 – 196 °C)	3.0	[3]
PPGA6.2	Aluminum	Hot-pressing (175 °C, 0.5 MPa, 3 min)	15.4	This work
PP-g-MA	Aluminum	Hot-pressing (220 °C, 0.5 MPa, 10 min)	10.6	[4]
C_3-*co*-C_6-*co*-C_6OH	Aluminum	Hot-pressing (180 °C, 2 MPa, 5 min)	8.0	[5]
DOMA-EHMA	Aluminum	Pressing with pair of metal clamps at 70 °C, 60 min	5.8	[2]

Table S2. Summary of lap shear strength comparing between this work and previous studies. (continued)

Adhesives	Substrates	Bonding method	Lap shear strength (MPa)	References
PPGA8.9	Stainless steel	Hot-pressing (175 °C, 0.5 MPa, 3 min)	18.3	This work
3M™ 3747	Stainless steel	Hot-melt adhesive (177 – 196 °C)	2.8	[3]
PP_{DEOA}	Steel	Hot-pressing (180 °C, 197 $kN_{normal\ force}/mm^2$, 5 min)	17.4	[6]
C_3-*co*-C_6-*co*-C_6OH	Stainless steel	Hot-pressing (180 °C, 2 MPa, 5 min)	16.7	[5]
PPGA8.9	Copper	Hot-pressing (175 °C, 0.5 MPa, 3 min)	8.5	This work
DOMA-EHMA	Copper	Pressing with pair of metal clamps at 70 °C, 60 min	6.3	[2]
3M™ 3748VO	FR-4**	Hot-melt adhesive (177 – 196 °C)	1.4	[7]

*Substrate failure, **A copper laminated circuit board

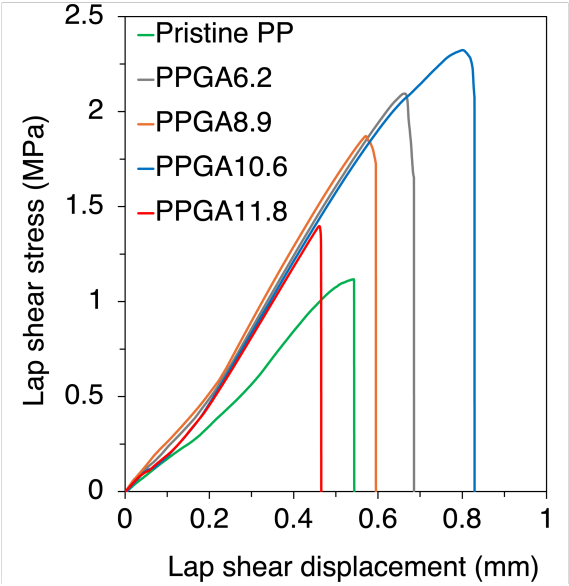

Figure S20. Lap-shear stress and displacement curves of pristine PP and PPGA adhesives on PP substrate after immersion in water at 60 °C for 7 days.

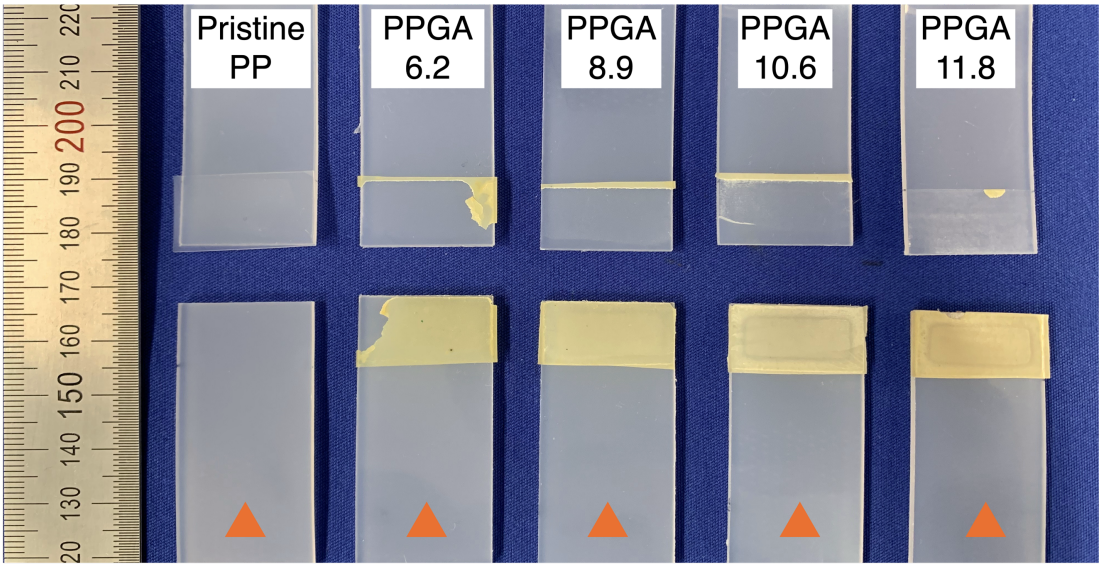

Figure S21. Failure modes (▲ = adhesive failure) of single lap-shear specimens after immersion in water at 60 °C for 7 days for PP substrate bonded with each adhesive.

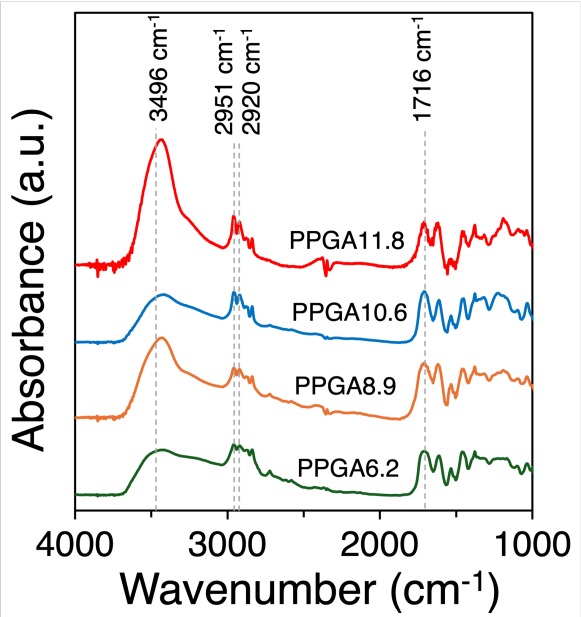

Figure S22. FTIR spectra of PPGAs after immersion under water for 7 days.

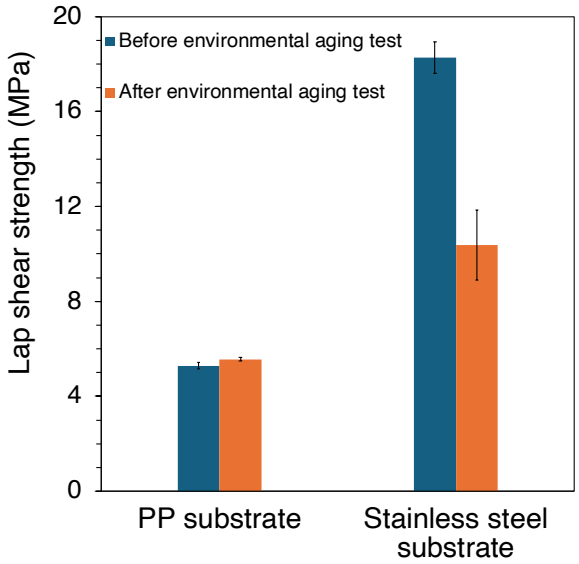

Figure S23. Comparison of lap-shear strength on PP and stainless steel substrates before and after environmental aging test.

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