

Biomimetic Hot-Melt Adhesive Using Galloyl-Grafted Polypropylene for Multisubstrates

Paripat Kraisornkachit, Mika Mano, Kiyotaka Hitomi, Shin Horiuchi, and Masanobu Naito*

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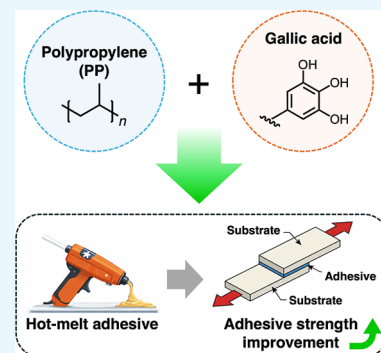
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ABSTRACT: Hot-melt adhesives (HMAs) are widely used in packaging, electronics, and automotive applications, but their adhesion to low-surface-energy polymers, such as polypropylene (PP), remains challenging. Here, we present a simple and scalable method to prepare galloyl-grafted polypropylene (PPGA) by introducing a gallic acid-bearing methacrylate onto PP through a peroxide-initiated process. The resulting hot-pressed adhesive PP films exhibited exceptionally high lap-shear strengths across various substrates. PPGA-based adhesives achieved substrate failure on PP, indicating that interfacial adhesion surpassed the cohesive strength of the substrate because of molecular interdiffusion and fusion of amorphous PP chains at the interface. On metal substrates, the adhesives reached record-high lap-shear strengths up to 18.3 MPa on stainless steel, far exceeding those of pristine PP. Furthermore, PPGA maintained significant bonding strength on PP and stainless steel even after 7 days of water immersion or UV aging, demonstrating excellent wet adhesion and long-term stability. This study establishes galloyl-grafted polypropylene as a high-performance, multisubstrate hot-melt adhesive with outstanding dry and wet adhesion, thereby offering a practical, scalable, and sustainable alternative to conventional hot-melt adhesives.

KEYWORDS: polypropylene, gallic acid, hot-melt adhesive, lap-shear strength, wet adhesion



1. INTRODUCTION

Hot-melt adhesives (HMAs) are thermoplastic materials that melt upon heating and solidify upon cooling, enabling rapid, solvent-free bonding of plastics, metals, and other substrates. Their advantages—rapid processing, the absence of volatile organic compounds (VOCs), and high production efficiency—have made them indispensable in packaging, electronics, and automotive applications.^{1–6} However, most commercial HMAs, such as ethylene–vinyl acetate and polyurethane, exhibit limited adhesive strength, typically around 6–7 MPa.⁷ Therefore, enhancing the adhesion performance of HMAs remains a significant challenge.

Polypropylene (PP) is one of the most widely used thermoplastics because of its low cost, lightweight, durability, and chemical resistance.⁸ Despite these benefits, PP exhibits inherently poor adhesion to itself and to other materials owing to its low surface energy, nonpolar nature, and lack of reactive functional groups.^{9–11} Numerous approaches have been explored to improve PP adhesion, including welding techniques, surface treatments, and chemical modifications.^{12–20} Among these, functionalization with polar groups represents one of the most direct and effective strategies. Maleic anhydride (MAH) grafting, for example, has been widely used and shown to enhance bonding strength with metals such as aluminum.^{21–25} More recently, hydroxyl-functionalized polypropylene adhesives have achieved shear strengths exceeding 16 MPa on steel,^{7,26} although these

methods often require expensive catalysts or complex polymerization processes. Hence, a simple and scalable approach to imparting strong adhesive functionality to PP is still highly desirable.

Bioinspired strategies have recently gained attention as a means of achieving strong and versatile adhesion. Catechol groups, derived from dopamine, interact strongly with a wide range of substrates—including metals, glass, and plastics—and retain adhesion even under wet conditions.^{27–32} Gallic acid, a natural phenolic compound bearing a pyrogallol moiety (a benzene ring with three adjacent hydroxyl groups), offers even greater functionality. Galloyl-functionalized polymers have been shown to outperform catechol-based systems in both dry and wet adhesion, achieving higher lap-shear and peel strengths.^{33–37} However, despite these advances, the incorporation of galloyl functionalities into nonpolar thermoplastics such as polypropylene has not been explored, leaving their potential for high-performance, scalable adhesives untested.

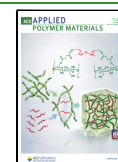
In this study, we report the first development of galloyl-grafted polypropylene (PPGA) for hot-melt adhesive applica-

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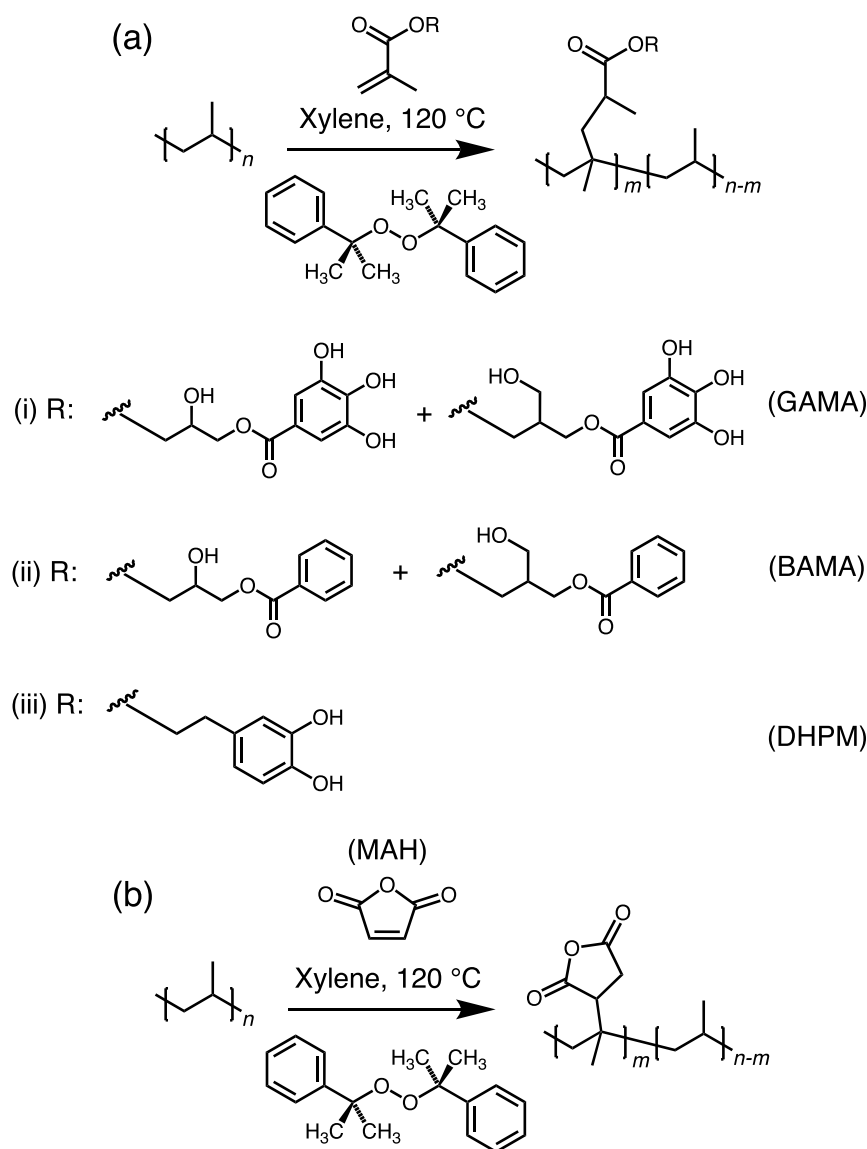
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Scheme 1. Synthesis Routes of (a) Galloyl-, Benzoyl-, and Catechol-Functionalized Polypropylenes (PPGA, PPBA, and PPCA) and (b) Maleic Anhydride-Grafted Polypropylene (PPMA) Using Dicumyl Peroxide (DCP) as the Initiator in Xylene at 120 °C^a



^aIn (a), three types of methacrylate monomers were grafted onto the polypropylene backbone: (i) GAMA, bearing a pyrogallol-type galloyl group with three adjacent hydroxyl substituents; (ii) BAMA, containing a benzoyl group without hydroxyl functionalities; and (iii) DHPMA, introducing a catechol-type dihydroxyphenyl group. (b) Shows the conventional grafting of maleic anhydride (MAH) onto polypropylene for comparison.

tions. By grafting a gallic acid-bearing methacrylate (GAMA) onto the pristine PP through a simple peroxide-initiated grafting process, followed by hot pressing, we obtained the GAMA-grafted PP films exhibiting significantly enhanced adhesive performance. The adhesion properties of these films were systematically evaluated on both low-surface-energy PP substrates and high-surface-energy metal substrates (aluminum, stainless steel, and copper) under dry and wet conditions. The results demonstrate record lap-shear strengths compared to previously reported PP-based hot-melt adhesives, highlighting galloyl functionalization as a simple, scalable, and highly effective strategy for next-generation hot-melt adhesives.

2. MATERIALS AND METHODS

2.1. Materials

PP pellets (F-704NP, Prime Polymer Co., Ltd., Tokyo, Japan) were used as pristine polymers, and their physical properties are listed in Table S1. Gallic-acid-bearing methacrylate (GAMA; NOF Corporation, Tokyo, Japan) was used as received. Dicumyl peroxide (Nacalai Tesque, Inc., Kyoto, Japan) served as a radical initiator. Xylene (FUJIFILM Wako Pure Chemical Corp., Osaka, Japan) was used as a solvent, and methanol (Nacalai Tesque, Inc., Kyoto, Japan) was employed for precipitation and washing. Benzoic acid was obtained from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Glycidyl methacrylate, super dehydrated acetonitrile, sodium chloride, and potassium carbonate were obtained from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). Triethylamine and dichloromethane were obtained from Kanto Chemical Co., Inc. (Tokyo, Japan). Ethyl acetate and hexane were obtained from Nacalai Tesque, Inc. (Kyoto, Japan). 3,4-Dihydroxyphenethyl methacrylate (DHPM)

was obtained from Osaka Organic Chemical Industry Ltd. (Osaka, Japan) and used as received. Maleic anhydride (MAH) was purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan) and used as received. Polypropylene (100 × 25 × 2 mm), aluminum alloy A6061P-T6, stainless steel SUS304 (2B), and copper C1100P (100 × 25 × 1.5 mm) were obtained from Standard Testpiece (Kanagawa, Japan) and used as the substrates.

2.2. Modification of PP

A pristine PP pellet (1 g, 1 equiv) was placed in a 100 mL vial together with GAMA (1.48 g, 0.2 equiv) and dicumyl peroxide (360 mg, 0.06 equiv), and xylene (20 mL) was added as the solvent. The mixture was stirred under a nitrogen atmosphere at 120 °C for 8 h using a magnetic stirrer. After cooling to room temperature under nitrogen, the reaction mixture was poured into an excess amount of methanol to remove unreacted GAMA and residual dicumyl peroxide. The resulting PPGA was collected by suction filtration and dried under reduced pressure at 60 °C overnight (Scheme 1a). The same modification procedure was applied using 0.4, 0.6, and 0.8 equiv of GAMA. The obtained PPs modified with GAMA were designated as PPGAXX, where XX corresponds to the mole percentage of incorporated GAMA into the pristine PP (i). The actual incorporation ratios of the functional groups were determined by elemental analysis, as described in detail later. In this study, to investigate the effect of adjacent hydroxyl groups in the galloyl moiety, benzoyl methacrylate (BAMA)(ii) and 3,4-dihydroxyphenethyl methacrylate (DHMP)(iii) were employed as model compounds of GAMA, representing analogs without hydroxyl groups and with two adjacent hydroxyl groups, respectively. PPBA was synthesized using 0.4 equiv of BAMA relative to PP, following the same procedure as that for PPGA (Scheme 1a). Similarly, PPCA was prepared by introducing 3,4-dihydroxyphenethyl methacrylate (DHMP) into the pristine PP (Scheme 1a). Finally, maleic anhydride (MAH)-modified PP (PPMA) was prepared using 0.4 equiv of MAH relative to PP (Scheme 1b). A summary of the specimens prepared for adhesive testing is provided in Table 1. The preparation and characterization of

were determined by high-temperature gel permeation chromatography (HT-GPC, HLC-8321GPC, Tosoh, Japan) at 150 °C in dichlorobenzene, calibrated with Tosoh PStQuick polystyrene standards (Kits A–C). Fourier transform infrared (FTIR) spectra were recorded on a FT-IR 6100 (JASCO, Japan) using KBr pellets. Differential scanning calorimetry (DSC)(DSC-60 Plus, Shimadzu, Japan) was conducted at a heating/cooling rate of 10 °C min^{−1} from room temperature to 220 °C, down to −50 °C, and reheated to 220 °C. Data from the second heating cycle were used to calculate the degree of crystallinity (X_c) according to eq 1. ΔH_m is the measured enthalpies of melting obtained from DSC measurement, and ΔH_m^0 is the heat of fusion of the crystalline, assuming $\Delta H_m^0 = 209 \text{ J g}^{-1}$.^{7,38}

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (1)$$

The mechanical properties of bulk polypropylene samples were evaluated using a tensile tester (Autograph AG-X Plus, Shimadzu) at a crosshead speed of 2 mm min^{−1}. X-ray diffraction (XRD) was performed from $2\theta = 7.5$ – 32.5° to evaluate crystallinity with a MiniFlex600-C (Rigaku, Japan). The interfaces between the adhesive and adherend were investigated using scanning transmission electron microscopy (STEM) with a TECNAI Osiris scanning transmission electron microscope (FEI, Hillsboro, OR, USA) at an acceleration voltage of 200 kV. For the observation of the lamellar structures of PP and PPGA, the samples were stained with RuO₄ vapor for 8 h at 50 °C and then cut into approximately 100 nm thick sections using an ultramicrotome (Leica Ultracut UCT, Germany).

2.4. Single-Lap-Shear Test

Thin films of pristine PP and PPGA were prepared by hot-pressing at 175 °C and 10 MPa for 5 min between stainless steel plates lined with PTFE sheets. The resulting films measured $12.5 \pm 0.5 \times 25.0 \pm 0.5 \text{ mm}^2$ with a thickness of $0.18 \pm 0.03 \text{ mm}$. PPBA, PPCA, and PPMA were also prepared by the same procedure as PPGA. The specimens for lap-shear test were assembled by placing the hot-melt adhesive between PPs or metal substrates (Figure S5). The overlapping area matched the film dimensions. The specimens were hot-pressed using spacers of equal thickness. PP substrate specimens were bonded at 160 °C and 0.5 MPa for 3 min to avoid substrate melting, while metal specimens were bonded at 175 °C under the same pressure and duration (Figure S6). It should be noted that, for adhesion to the PP substrate, the hot-pressing temperature (160 °C) was set close to the melting point (T_m) of the hot-melt adhesive, but lower than that of the PP substrate as $T_m = 168.9 \text{ °C}$ (Figures S7 and S8) to ensure melting of the adhesive film without deforming the substrate. Single-lap-shear tests were performed using an Autograph AG-X Plus tensile tester (Shimadzu, Japan) at a crosshead speed of 1 mm min^{−1}. Lap-shear strength was calculated as the maximum load divided by the overlap area, and displacement was determined as the elongation at fracture. At least five specimens were tested for each condition, and average values with standard deviations were reported.

2.5. Wet Adhesion and Stability under Environmental Aging Test

PP and stainless steel specimens for the lap-shear test were immersed in deionized water at 60 °C for 7 days. After immersion, the specimens were removed, the surface water was carefully wiped off, and lap-shear tests were performed using a tensile tester (Autograph AG-X Plus, Shimadzu, Japan) at a crosshead speed of 1 mm min^{−1}. For each adhesive, five specimens were tested, and the average lap-shear strength, together with the standard deviation, was reported. Additionally, the stability under environmental aging test was conducted for PPGA8.9 adhesive on PP and stainless steel substrates according to the test standard of JIS K7350-2-10 (BST). The samples were exposed to repeated cycles of UV irradiation (300–400 nm) and water spray with a black panel temperature of 63 °C and relative humidity of $50 \pm 10\%$ for 7 days. After that, the specimens underwent a lap-shear test with the same conditions as mentioned above. For each substrate, three specimens were tested, and the average lap-shear strength, together with the standard deviation, was reported.

Table 1. Summary of Hot-Melt Adhesive Samples Prepared with Different Modifications

sample name	grafting reagent	grafting reagent ratio (mol %)	PP F-704NP (mole equiv to PP)	grafting reagent (mole equiv to PP)	dicumyl peroxide (mole equiv to PP)
pristine PP	–	0	1	0	0
PPGA6.2	GAMA	15.9	1	0.2	0.06
PPGA8.9	GAMA	27.5	1	0.4	0.06
PPGA10.6	GAMA	36.2	1	0.6	0.06
PPGA11.8	GAMA	43.1	1	0.8	0.06
PPBA	BAMA	27.5	1	0.4	0.06
PPCA	DHMP	27.5	1	0.4	0.06
PPMA	MAH	27.5	1	0.4	0.06

BAMA, PPBA, PPCA, and PPMA are reported in the Supporting Information (Figures S1–S4). To comply with industrial and scalable processing protocols, a PPGA hot-melt adhesive with a grafting reagent ratio of 15.9 mol % was prepared using a reactive extrusion (REX) process and was abbreviated as PPGA-REX. The extrusion was carried out in a twin-screw extruder (MC 15 HT, Xplore, The Netherlands). The extrusion temperature was set to 190 °C. After thorough mixing, the polymer melt was extruded and pelletized using a Pro Pelletizer (Xplore, The Netherlands). The resulting pellets were subsequently dried following the same procedure described above.

2.3. Characterization

Elemental analysis (UNICUBE, Elementar, Germany) was performed using temperature-programmed desorption gas chromatography with a TCD detector to quantify hydroxyl and carbonyl incorporation. Weight-average molecular weight (M_w) and polydispersity index (D)

Table 2. Summary of Characterization of Pristine PP/Grafted PPs

sample name	preparation ratio (mol %)	incorporation ratio ^a (mol %)	$M_w^b \times 10^3$ (g·mol ⁻¹)	D^b	T_m^c (°C)	X_c^c (%)
pristine PP ^d	0	0	308.4	4.4	161.6	52.7
PPGA6.2	15.9	6.2	331.7	3.7	165.7	32.5
PPGA8.9	27.5	8.9	321.0	3.1	165.7	23.9
PPGA10.6	36.2	10.6	350.0	3.9	165.8	17.1
PPGA11.8	43.1	11.8	344.5	4.4	167.4	10.0
PPBA	27.5	-	262.3	3.5	157.2	41.4
PPMA	27.5	-	94.0	2.6	154.0	37.9
PPCA	27.5	-	389.2	4.9	163.9	39.0

^aDetermined by elemental analysis. ^bDetermined by high-temperature gel permeation chromatography. ^cDetermined by DSC. ^dPristine PP was used as a control sample.

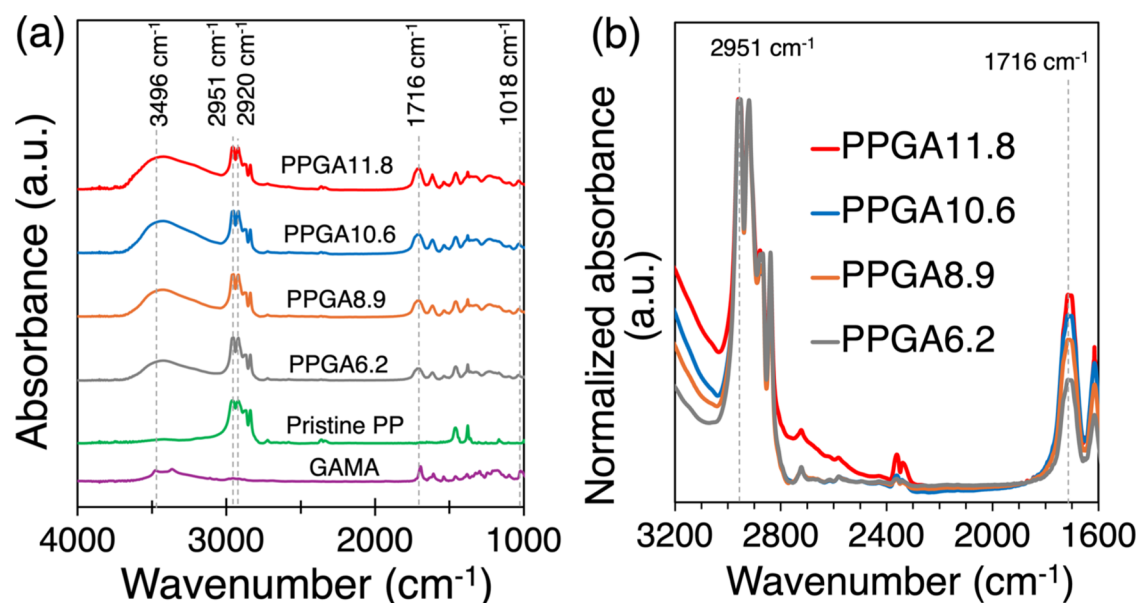


Figure 1. (a) FTIR spectra of GAMA, pristine PP, and PPGA. (b) Normalized FTIR spectra of PPGA samples showing increasing carbonyl band intensity at 1716 cm⁻¹.

3. RESULTS AND DISCUSSION

3.1. Characterization of Modified PPs

The results of the polymer modification are summarized in Table 2. The incorporation ratio of the galloyl group was calculated from the oxygen-to-carbon (O/C) ratio obtained by elemental analysis. The incorporation ratios of the PPGA series were determined to be 6.2, 8.9, 10.6, and 11.8 mol % for samples synthesized with the GAMA-to-PP molar feed ratios of 0.2, 0.4, 0.6, and 0.8, respectively. The samples are termed PPGA6.2, PPGA8.9, PPGA10.6, and PPGA11.8 according to these incorporation levels. The direct correlation between the feed ratio and the incorporated galloyl content clearly confirms the successful and controllable grafting.

FTIR spectroscopy (Figure 1a) further verified the incorporation of galloyl groups. The PPGA samples exhibited a broad O–H stretching band at 3496 cm⁻¹ that was absent in pristine PP, along with characteristic peaks at 1716 cm⁻¹ (C=O stretching) and 1018 cm⁻¹ (aromatic C–H out-of-plane bending).^{39–41} In contrast, pristine PP showed only intense CH₃ and CH₂ stretching bands at 2951 cm⁻¹ and 2920 cm⁻¹, respectively.⁴² The normalized spectra (Figure 1b) revealed a monotonic increase in the C=O peak intensity at 1716 cm⁻¹ with increasing GAMA incorporation, confirming a higher grafting degree of the galloyl-bearing methacrylate. FTIR

spectroscopy of the PPGA adhesive with a grafting ratio of 15.9 mol % prepared by the reactive extrusion (REX) exhibited the identical characteristic peaks as mentioned previously, indicating the successful synthesis of PPGA-REX adhesive by the REX method (Figure S9).

The DSC thermograms (Figures 2a and S10) revealed that the melting temperatures (T_m) of the PPGAs were slightly higher than that of pristine PP, whereas PPBA and PPMA exhibited marginally lower T_m values. Despite their reduced crystallinity (20–40% lower than pristine PP; Table 2 and Figure 2b), the PPGAs displayed elevated melting points, likely due to intermolecular hydrogen bonding, π – π stacking, and CH– π interactions among galloyl moieties in the amorphous phase. XRD analysis (Figure 2c) showed a decrease in crystallinity with increasing galloyl content, as indicated by the reduced intensity of α -phase reflections ($\alpha(110)$, $\alpha(040)$, $\alpha(130)$, and $\alpha(111)$) and a slight shift of the diffraction peaks to lower 2θ values. These results suggest that the bulky galloyl groups disrupt regular chain packing, leading to an increased amorphous fraction and altered crystal lattice spacing. Similar behavior was observed for PPCA, while PPMA and PPBA exhibited decreased T_m compared to pristine PP (Figure S11). Collectively, these results indicate that the polyphenolic groups promote secondary intermolecular interactions that compensate for the reduced crystallinity, thereby slightly elevating T_m .

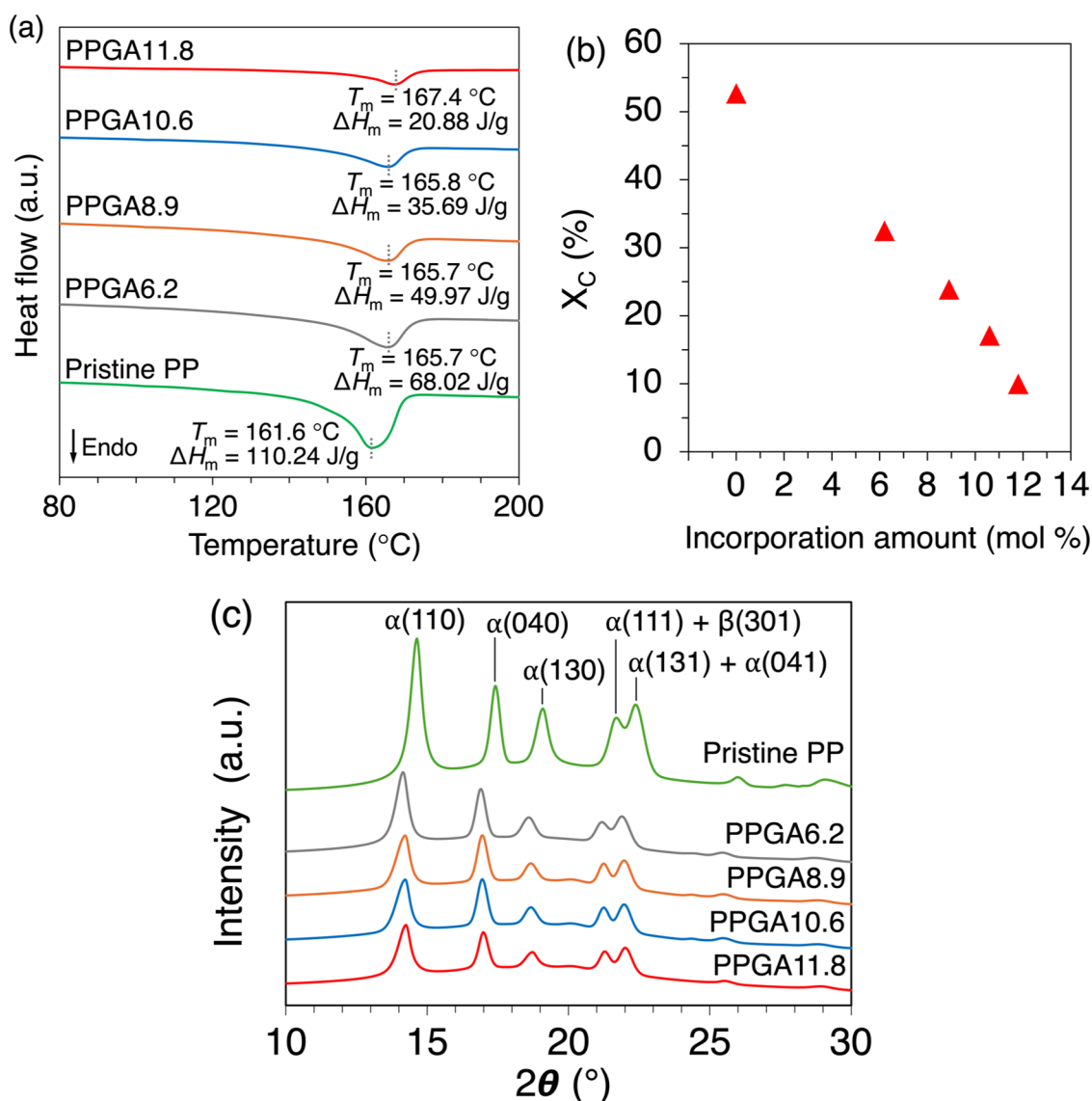


Figure 2. (a) DSC thermograms (second heating scan) of pristine PP and PPGAs, showing melting transitions and enthalpy of melting and (b) degree of crystallinity of PPGAs plotted as a function of the incorporation amount of GAMA. (c) XRD diffraction patterns of pristine PP and PPGAs.

Thin adhesive films were successfully fabricated at 175 °C (Figure S12).

The molecular characteristics of the PPs were analyzed by high-temperature GPC, as summarized in Table 2. The weight-average molecular weights (M_w) of the PPGAs were consistently higher than that of pristine PP ($308.4 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$), increasing with galloyl incorporation to $331.7\text{--}350.0 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$. The polydispersity index (D) remained comparable (3.1–4.4), indicating that the grafting reaction proceeded in a controlled manner without extensive branching or cross-linking. Notably, this behavior contrasts with the conventional maleic anhydride (MAH) grafting, where peroxide-initiated β -scission reactions cause severe chain cleavage, leading to reduced molecular weight and degraded mechanical performance.^{43,44} In the present system, no β -scission was observed, as evidenced by the stable M_w values of PPGA, PPBA, and PPCA, whereas PPMA showed a pronounced decrease to $94.0 \times 10^3 \text{ g} \cdot \text{mol}^{-1}$. Previous studies have shown that electron-rich, unsymmetrical monomers such as styrene can act as efficient radical acceptors, stabilizing

intermediate radical species and promoting grafting over chain scission. The aromatic ring in styrene enhances radical delocalization, increasing grafting efficiency while suppressing β -scission. In our study, gallic-acid-bearing methacrylate (GAMA) contains a benzene ring and an unsymmetrical structure, providing the same benefits as styrene.^{45–47} Therefore, GAMA exhibits better reactivity toward free-radical grafting, which minimizes PP degradation. These results clearly demonstrate that galloyl grafting preserves the backbone integrity of PP, offering a controlled and degradation-free grafting route to functionalized polypropylene without compromising molecular weight.

3.2. Adhesion Performance on Polypropylene Substrates

The adhesion performance of the synthesized adhesives on PP substrates was evaluated by single-lap-shear tests (Figure 3a). Specimens bonded with pristine PP adhesive exhibited a lap-shear strength of 2.2 MPa, limited by interfacial polymer entanglement formed in the molten state and mechanically anchored upon cooling. The fracture surface (Figure 3b)

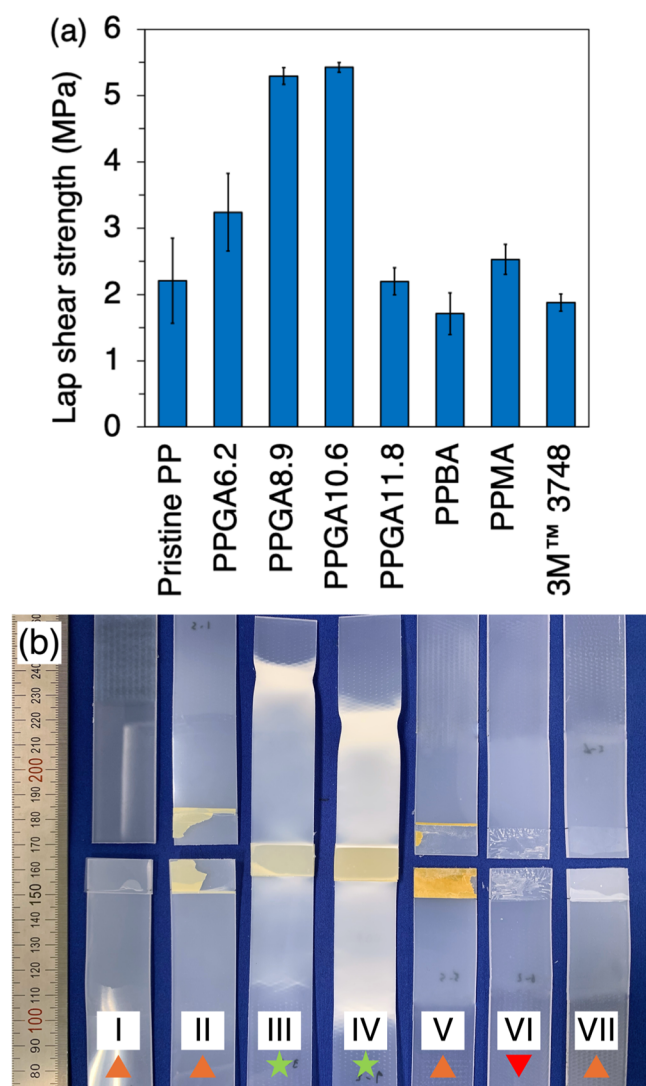


Figure 3. (a) Lap-shear adhesion strength of pristine PP, PPGA, PPBA, PPMA, and 3 M 3748 adhesives on PP substrate. Error bars represent standard deviation. (b) Failure modes (▲ = adhesive failure, ★ = substrate failure, and ▼ = cohesive failure) of single lap-shear specimens for PP substrate bonded with each adhesive (I = Pristine PP, II = PPGA6.2, III = PPGA8.9, IV = PPGA10.6, V = PPGA11.8, VI = PPMA, and VII = PPBA).

showed complete adhesive failure, confirming the absence of chemical bonding. In contrast, PPGA adhesives displayed markedly enhanced adhesion. PPGA6.2 achieved 3.2 MPa, attributed to hydrogen bonding via hydroxyl and carbonyl groups introduced by galloyl grafting. Increasing the functional group incorporation to 8.9 and 10.6 mol % raised the lap-shear strength to 5.3 and 5.4 MPa, respectively, leading to substrate failure characterized by necking and whitening of the PP substrate. The stress–displacement curves (Figure S13) indicated that the applied shear stress approached or exceeded the yield strength of the PP substrate, confirming interfacial adhesion stronger than the cohesive strength of PP.

The adhesion enhancement arises from two synergistic effects: (1) the introduction of polar functional groups that enable hydrogen bonding and dipole interactions, and (2) reduced crystallinity that increases amorphous chain mobility, facilitating interdiffusion at the interface. XRD analysis (Figure 2c) confirmed decreased crystallinity and a shift of α -phase

peaks to lower 2θ angles, consistent with disrupted chain packing by the bulky galloyl groups. The resulting amorphous phase promotes fusion between adhesive and substrate chains during hot pressing, yielding a mechanically integrated interface. Therefore, adhesion on PP substrates is governed by chain interdiffusion and recrystallization-induced anchoring. At excessive galloyl incorporation (11.8 mol %), the lap-shear strength dropped back to 2.2 MPa, accompanied by adhesive failure. Tensile tests revealed reduced ductility with increasing galloyl content (fracture strain decreasing from 30.1% to 8.5%; Figure S14), indicating that excessive polar functionalization leads to brittleness and stress localization. Thus, balancing brittleness and ductility is a critical factor for adhesion performance.^{48,49} These findings emphasize the importance of balancing interfacial bonding and bulk ductility to achieve optimal adhesion.

For comparison, other functional groups were grafted onto PP in this study. PPBA, PPCA, and PPMA were synthesized and investigated for the lap-shear adhesion strength. The fabrication of their hot-melt adhesive films and lap-shear specimens followed the same procedure as that for PPGA. The resulting lap-shear adhesion strengths are shown in Figure 3a. PPBA and PPMA exhibited lap-shear strengths of 1.7 and 2.5 MPa, respectively, indicating the poor adhesion properties compared with PPGAs.

However, the PPCA sample exhibited no adhesion. This failure is likely attributable to a poor grafting reaction, evidenced by macroscopic observations (Figure S12) showing the hot-melt adhesive film to contain an incompatible phase and possess a distinct brown color. The observed brown coloration is consistent with the oxidation of the catechol functional groups with dicumyl peroxide, which leads to the formation of quinone species. This oxidative instability was verified by UV/vis spectroscopy; when DHPM was mixed with dicumyl peroxide at 100 °C for 20 h, the peak intensity for quinone at 450 nm significantly increased (Figure S15a). Conversely, the GAMA exhibited better stability without showing quinone formation under the identical conditions (Figure S15b). Macroscopic observation of these aging experiments further supported this finding (Figure S15c), DHPM transitioned from transparent to dark brown, while GAMA slightly changed in color, confirming the superior stability of the GAMA structure.

3.3. Interfacial Analysis

The interfacial region between the PP substrate and the PPGA adhesives was examined by using STEM to elucidate the structural features responsible for the enhanced adhesion (Figure 4). Distinct interfacial layers were observed in both PPGA6.2 and PPGA10.6, indicating effective interdiffusion and partial fusion between the molten adhesive and the PP substrate during hot pressing. In both cases, a crystalline lamellar structure was detected near the interface, reflecting the recrystallization of the polymer chains upon cooling. However, notable morphological differences were found to depend on the galloyl content.

For PPGA6.2, the interfacial region exhibited a dense lamellar morphology extending continuously from the substrate into the adhesive layer (Figure 4a). This structure suggests that moderate galloyl incorporation preserves chain regularity, allowing partial crystallization and the formation of interpenetrating lamellae that mechanically anchor the adhesive to the substrate. In contrast, PPGA10.6 displayed a

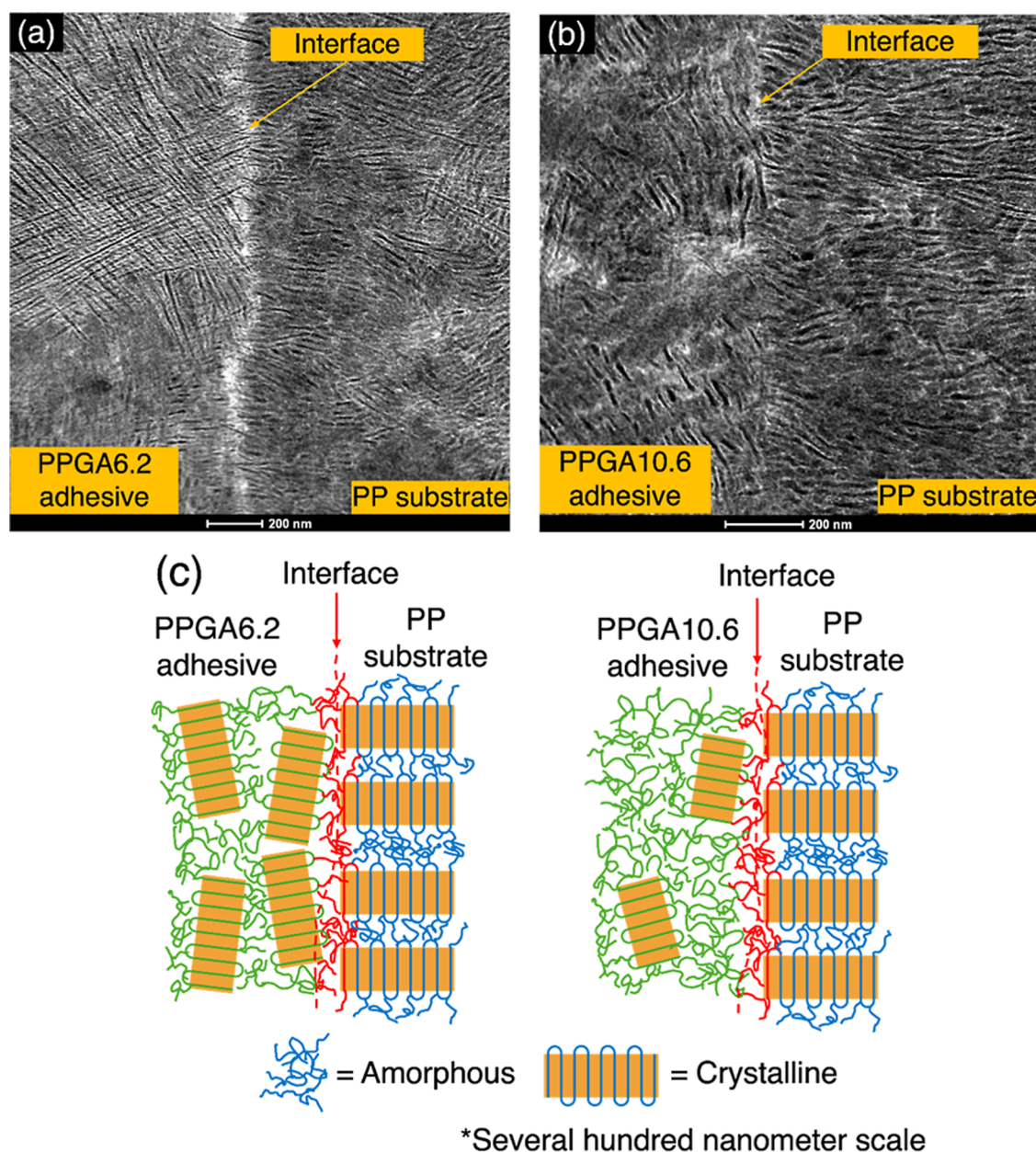


Figure 4. STEM images of the interfacial region between PP substrate and (a) PPGA6.2 adhesive and (b) PPGA10.6 adhesive. (c) Illustration of the interfacial lamellar structure for each adhesive.

significantly broader amorphous interphase with a lower density of lamellar structures (Figure 4b). The increased galloyl functionalization introduces bulky side groups and polar interactions that disturb the regular packing of polypropylene chains, thereby inhibiting crystalline growth and enhancing the amorphous fraction. The amorphous layer formed at the interface acts as a viscoelastic “soft bridge” that accommodates mechanical deformation, distributing stress more evenly across the joint. This viscoelastic region facilitates chain slippage and energy dissipation under load, contributing to higher adhesive toughness and resistance to interfacial failure. These observations are consistent with the DSC and XRD results (Figure 2b,c), which revealed a systematic reduction in crystallinity with increasing galloyl content. The decrease in crystallinity correlates with enhanced chain mobility, enabling greater interdiffusion between the molten adhesive and the PP substrate during bonding. At the same time, intermolecular

hydrogen bonding and π – π interactions among galloyl moieties contribute to cohesive strength within the adhesive phase. Consequently, the interfacial adhesion arises from the combination of physical chain interdiffusion and localized intermolecular interactions, producing a well-integrated and mechanically stable interface.

A schematic representation of this interfacial structure is provided in Figure 4c. At lower galloyl content (PPGA6.2), the interface is dominated by lamellar interlocking and partial crystallization, leading to mechanical anchoring but limited stress relaxation. At higher galloyl incorporation (PPGA10.6), the interphase transitions into a semiamorphous layer that enhances stress dissipation and adhesion strength. However, excessive functionalization further disrupts molecular packing and reduces ductility, leading to brittle failure, as observed in the mechanical tests (Figure S14). These results clearly demonstrate that the optimized interfacial architecture—

characterized by a balanced combination of crystalline anchoring and amorphous flexibility—is critical for achieving strong and durable adhesion in galloyl-functionalized polypropylene systems.

3.4. Adhesion Performance on Metal Substrates

The adhesion of the synthesized adhesives was further examined on aluminum, stainless steel, and copper substrates, which possess higher surface energies than PP as indicated by their lower contact angles (Figure S16). The surfaces of the metal substrates were treated prior to the preparation of the lap-shear specimens according to the procedure described in the Supporting Information. Bonding was conducted using a hot press at 175 °C and 0.5 MPa for 3 min to ensure complete melting of the adhesive films. As shown in Figure 5, PPGA

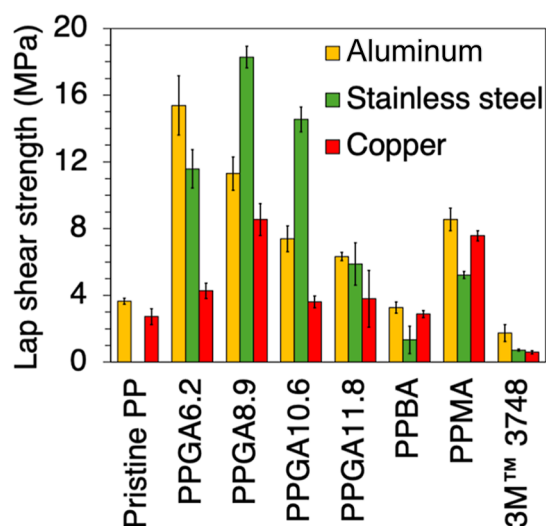


Figure 5. Lap-shear adhesion strength of pristine PP, PPGA, PPBA, PPMA, and 3 M 3748 adhesives on metal substrates (aluminum, stainless steel, and copper). Error bars represent standard deviation.

adhesives exhibited drastically improved adhesion compared with pristine PP, which displayed negligible bonding to any metal substrate. For aluminum, the lap-shear strength increased from 3.6 MPa (pristine PP) to 15.4 MPa for PPGA6.2, owing to strong interfacial interactions between galloyl hydroxyl/carboxyl groups and surface hydroxyl groups on the native aluminum oxide layer. A similar trend was observed for stainless steel, where adhesion strength reached a maximum of 18.3 MPa at 8.9 mol % galloyl incorporation before declining at higher levels (14.5 MPa for PPGA10.6 and 5.9 MPa for PPGA11.8). For copper substrates, the maximum adhesion was achieved at the same composition (8.9 mol %), reaching 8.5 MPa, again followed by a decline with further functionalization. These results demonstrate that an optimal galloyl content of approximately 9 mol % yields the best adhesion performance across all metal substrates, balancing strong interfacial bonding with sufficient adhesive ductility. Comparative experiments using PPBA and PPMA adhesives further highlighted the critical role of hydroxyl groups. PPBA, which shares a similar backbone structure with PPGA but lacks hydroxyl functionality, showed significantly lower lap-shear strengths of 3.3, 1.3, and 2.9 MPa on aluminum, stainless steel, and copper, respectively. This clearly indicates that hydrogen bonding between galloyl hydroxyl groups and surface hydroxyls on metal oxides is essential for achieving high

adhesion. PPMA, containing maleic anhydride groups, displayed moderate adhesion (8.6 MPa on aluminum, 5.2 MPa on stainless steel, and 7.6 MPa on copper), which was notably inferior to PPGA8.9, suggesting that the galloyl functionality provides stronger and more versatile adhesion mechanisms than conventional anhydride grafting. PPCA, which contains catechol moieties susceptible to oxidative conversion into quinone structures during processing, exhibited no adhesion because the oxidation suppressed hydrogen-bonding capability of the catechol groups. The corresponding lap-shear stress–displacement curves are reported in Figure S17. Additionally, the PPGA-REX adhesive with a grafting ratio of 15.9 mol %, prepared via reactive extrusion (REX), exhibited a remarkable lap-shear strength of 16.7 MPa (Figure S18), highlighting the industrial applicability of the proposed PPGA adhesive. Furthermore, reusability was evaluated on stainless steel substrates for each PPGA adhesive. The results showed that the PPGA hot-melt adhesives maintained satisfied adhesion performance on the second cycle (Figure S19).

Fracture surface analysis (Figure 6) provided additional insight into failure modes. The pristine PP showed purely adhesive failure, with no residue on one substrate surface. In contrast, PPGA6.2 and PPGA8.9 exhibited cohesive failure, leaving adhesive residues on both sides, confirming robust interfacial bonding. However, adhesives with higher galloyl incorporation (≥ 10.6 mol %) reverted to adhesive failure, correlating with the observed decrease in lap-shear strength and reflecting increased brittleness of the adhesive films. These findings confirm that adhesion to metals is dominated by chemical interactions between galloyl hydroxyl/carboxyl groups and hydroxylated metal surfaces, while maintaining adequate ductility is crucial to prevent stress localization and interfacial debonding.

3.5. Structure–Property Relationships and Adhesion Mechanism

DSC and XRD analyses (Figure 2b,c) collectively demonstrate that galloyl functionalization disrupts crystalline ordering, leading to an increased amorphous phase and higher segmental mobility. This structural modification exerts two complementary effects on adhesion, depending on the substrate. For polymer–polymer bonding (PP substrate), the lower crystallinity facilitates molecular interdiffusion and fusion across the interface during hot pressing, followed by recrystallization that locks the interpenetrated chains in place, yielding strong cohesive bonding and substrate failure. In contrast, for polymer–metal bonding, the polar hydroxyl and carboxyl groups of the galloyl moieties engage in specific hydrogen bonding and coordination with surface hydroxyls on aluminum and stainless steel, producing strong chemical adhesion. However, at excessive galloyl concentrations, the increased polarity restricts chain motion and renders the adhesive brittle, resulting in a reduction in overall adhesion strength. These results indicate that galloyl functionalization endows PP-based hot-melt adhesives with a dual adhesion mechanism: physical interdiffusion and anchoring dominate on polymeric substrates, whereas chemical interactions control adhesion on metallic substrates. The balance between these two contributions is optimized at a galloyl incorporation ratio of approximately 8.9 mol %, at which both interfacial strength and bulk ductility are maximized. A detailed surface chemical

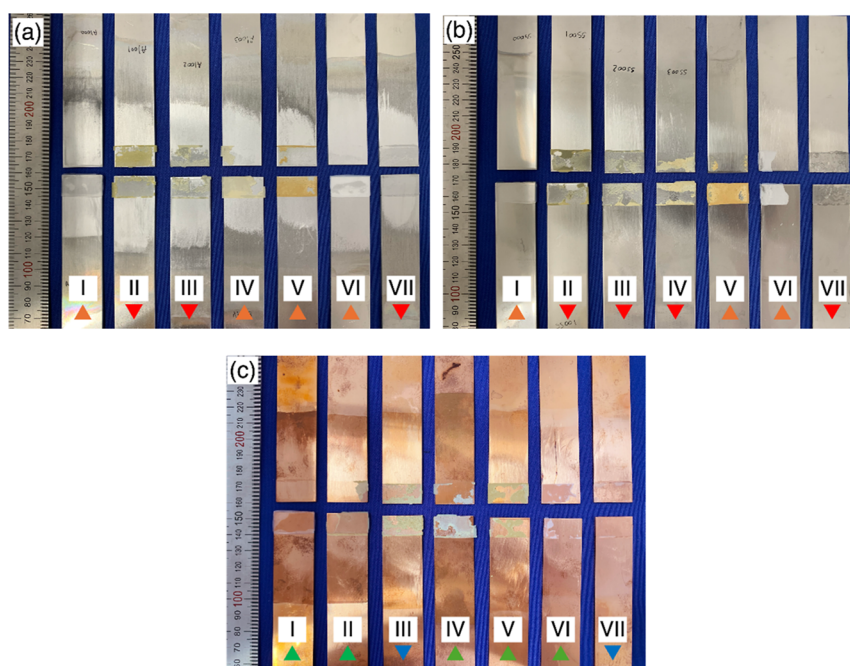


Figure 6. Failure modes (▲ = adhesive failure and ▼ = cohesive failure) of single lap-shear specimens for (a) aluminum substrate, (b) stainless steel substrate, and (c) copper substrate bonded with each adhesive (I = Pristine PP, II = PPGA6.2, III = PPGA8.9, IV = PPGA10.6, V = PPGA11.8, VI = PPBA, and VII = PPMA).

analysis to distinguish among these interaction mechanisms would be an interesting direction for future investigation.

As summarized in Table S2, the PPGA adhesives developed in this study exhibit the highest reported lap-shear strengths for aluminum and stainless steel among PP-based hot-melt adhesives, achieving up to 18.3 MPa under simple hot-pressing conditions. The combination of strong interfacial bonding and excellent substrate compatibility demonstrates that galloyl functionalization provides a versatile and scalable approach for enhancing the adhesion of PP substrate. Overall, the galloyl moiety provides an ideal balance of polarity and flexibility to unify interfacial and cohesive strength. This dual mechanism—physical interdiffusion with polymeric substrates and chemical bonding with metallic substrates—offers a general design principle for developing next-generation hot-melt adhesives with broad substrate applicability and superior performance.

3.6. Wet Adhesion and Stability under Environmental Aging Test Results

The introduction of galloyl-functionalized polymers significantly enhanced adhesion performance, even after water immersion. To evaluate this wet adhesion, specimens of stainless steel and PP substrates bonded with both pristine PP and PPGA adhesives were tested. The specimens were immersed in deionized water at 60 °C for 7 days, then dried and subjected to single-lap-shear tests. The results of the PP substrate are presented in Figure 7. A clear difference was observed between the adhesives, with pristine PP exhibiting the lowest lap-shear strength at 1.2 MPa, while PPGA10.6 achieved the highest at 2.3 MPa. In contrast, PPGA11.8 showed a lap-shear strength similar to that of pristine PP. This is likely due to the higher concentration of the polar galloyl-functional group, which may have led to a faster water absorption process. A comparison of adhesion performance before (Figure 3) and after (Figure 7) immersion reveals that lap-shear strength decreased by approximately 50% across all

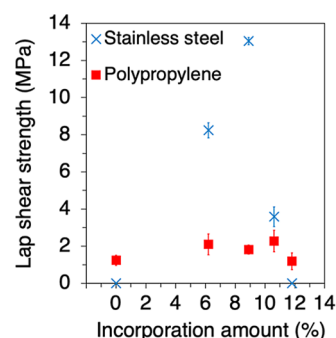


Figure 7. Lap-shear adhesion strengths of pristine PP and PPGA adhesives on stainless steel and PP substrate after immersion in water at 60 °C for 7 days. Error bars represent standard deviation.

adhesive polymers. The lap-shear stress and displacement curves of pristine PP and PPGA adhesives are reported in Figure S20. Notably, all specimens exhibited an adhesive failure mode after water immersion, as the adhesive film remained only on one side of the PP substrate (Figure S21). In the case of a stainless steel substrate, lap-shear strength exhibited satisfactory adhesion performance after immersion under water for 7 days (Figure 7). Despite a general decrease in strength after immersion, the galloyl-functionalized adhesives consistently retained superior adhesion, demonstrating their robustness in humid environments. This behavior was supported by FTIR spectra of the adhesives after 7 days of water immersion, which showed the retention of the broad O—H stretching band at 3496 cm^{-1} and the C=O stretching band at 1716 cm^{-1} (Figure S22). The polymers thus demonstrated satisfactory wet adhesion, positioning them as promising candidates for applications requiring water resistance. Regarding the environmental aging test results, the PPGA8.9 adhesive maintained satisfactory adhesion performance under severe aging conditions, retaining 57% of its original lap-shear

strength on stainless steel substrates (Figure S23). It also preserved substrate failure behavior on PP, characterized by necking and whitening of the PP substrate. These results demonstrate that the galloyl-functionalized system possesses sufficient thermal-oxidative and UV stability for demanding outdoor applications, effectively overcoming typical stability limitations.

4. CONCLUSIONS

In this study, we successfully synthesized galloyl-functionalized PP (PPGA) by grafting a gallic acid-bearing methacrylate onto PP through a simple peroxide-initiated process. The resulting hot-melt adhesive films demonstrated outstanding adhesion across multiple substrates. On PP substrates, PPGA adhesives achieved lap-shear strengths sufficient to cause substrate failure, far exceeding pristine PP and other functionalized PP adhesives. On metals, record lap-shear strengths were obtained, including 18.3 MPa on stainless steel, representing the highest values reported for PP-based hot-melt adhesives. The occurrence of substrate failure on the PP substrate indicates that the interfacial strength between the adhesive and the PP substrate exceeded the cohesive strength of the substrate itself. This behavior is attributed to the diffusion and fusion of amorphous PP chains at the interface during hot pressing, forming an interpenetrated interfacial layer reinforced by galloyl-induced hydrogen bonding, which effectively eliminates the distinct interface. Furthermore, PPGA maintained significant adhesion to PP even after 7 days of water immersion, highlighting its promising wet adhesion. These results establish galloyl-grafted PP as a simple, scalable, and high-performance hot-melt adhesive. By combining exceptional adhesion with a simple and scalable synthesis and bonding process, PPGA offers a practical and versatile alternative to current commercial adhesives for both polymeric and metallic substrates.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.6c01626>.

Physical properties of PP; preparation and characterization of other hot-melt adhesive materials; schematic illustrations of the specimen and apparatus; characterization of substrates; appearance of hot-melt adhesive films; stress–strain curves of lap-shear tests and adhesive films; characterization of stability; surface treatment of substrates; reusability test of hot-melt adhesives; comparison table of lap-shear strength; failure modes of wet adhesion specimens; FTIR spectra of adhesives after water immersion; and environmental aging test results (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Masanobu Naito — Research Center for Macromolecules and Biomaterials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan; Program in Materials Science and Engineering, Graduate School of Science and Technology, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan; orcid.org/0000-0001-7198-819X; Email: Naito.masanobu@nims.go.jp

Authors

Paripat Kraisornkachit — Research Center for Macromolecules and Biomaterials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan; Program in Materials Science and Engineering, Graduate School of Science and Technology, University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan; orcid.org/0000-0002-0796-3665

Mika Mano — Research Center for Macromolecules and Biomaterials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan

Kiyotaka Hitomi — Research Center for Macromolecules and Biomaterials, National Institute for Materials Science (NIMS), Tsukuba, Ibaraki 305-0047, Japan

Shin Horiuchi — Research Laboratory for Adhesion and Interfacial Phenomena (AIRL), Research Institute for Core Technology for Materials Innovation, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan; orcid.org/0000-0001-8256-0498

Complete contact information is available at:
<https://pubs.acs.org/doi/10.1021/acsapm.6c01626>

Notes

The authors declare no competing financial interest.

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