

Toward Sustainable Adhesives with Biodegradability, Scalability, and Removability: Poly(butylene succinate)-Based Hot-Melt Adhesives

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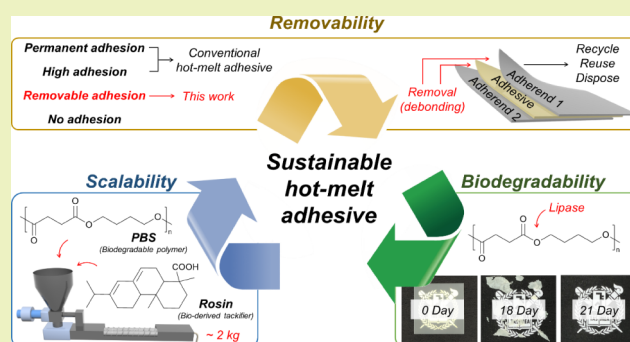
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ABSTRACT: Previous studies aiming to achieve sustainability in adhesive materials, primarily focused on the integration of bioderived or biodegradable components. However, existing sustainable adhesives often prioritize permanent adhesion over removability, which limits their recyclability. Herein, we introduce an innovative approach for producing scalable, biodegradable, and removable hot-melt adhesives, offering sustainability. Polybutylene succinate (PBS) was selected as the base polymer because of its excellent melt processability, biodegradability, and commercial availability. To impart adhesiveness, three biomass-derived tackifiers were incorporated; basic rosin, disproportionated rosin, and rosin ester. The use of a twin-screw extruder enabled the efficient mixing of the base polymer and tackifiers for large-scale production at the kilogram scale. Our investigation revealed that basic rosin exhibited optimal compatibility and wettability, which were attributed to its high acid value. The high acid value promoted rapid crystallization and minimized crystal defects. A correlation between the crystallization behavior and adhesion strength was also established, identifying the optimal composition. The optimal composition yields a satisfactory adhesion strength (2.5 N/25 mm) that makes it suitable for removable or repositionable adhesives. Additionally, our optimized adhesive exhibited sufficient biodegradability and was completely decomposed by lipase within 21 d, which has not been observed in previous sustainable hot-melt adhesive studies. This study provides a practical pathway for enhancing adhesive sustainability with the potential for further advancements in tailoring the adhesion strength for diverse applications in future research.

KEYWORDS: biodegradable polymer, rosin, crystallization behavior, adhesion, enzymatic degradation



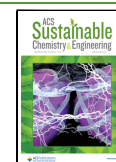
INTRODUCTION

Adhesives are polymer-based substances that adhere two distinct substrates together; they are traditionally employed in medical bandages, labels, and packaging materials.¹ Recently, their utility has extended to advanced sectors such as electronics^{2–4} and biomedical applications,^{5–7} fostering growth in the adhesive market, which is expected to reach \$93.3 billion by 2028.⁸ However, prevalent adhesives in current industries are derived from petroleum and are nonbiodegradable. Consequently, there is an increasing focus on the development of sustainable adhesive alternatives to address these nonenvironmentally friendly aspects.^{9–11}

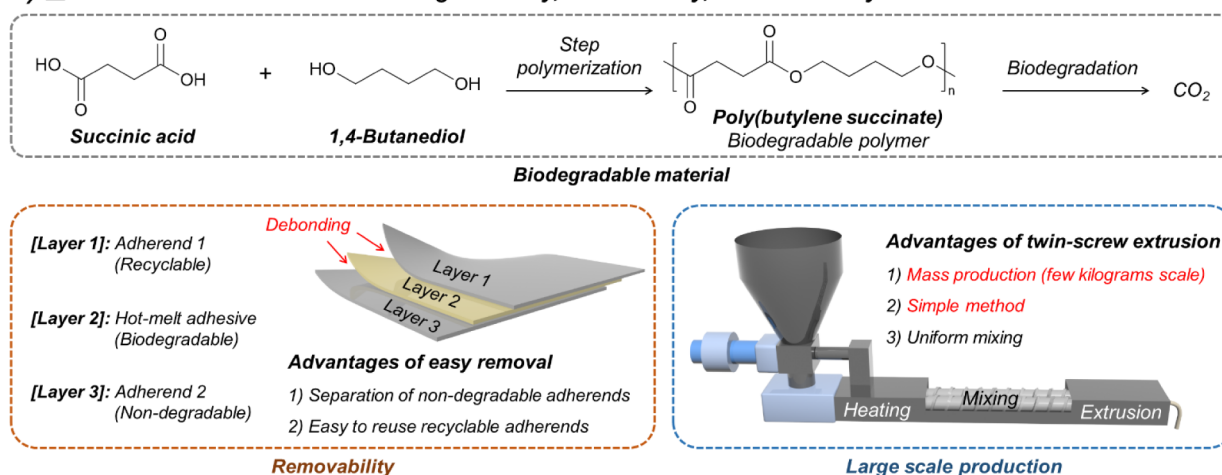
Sustainable adhesives have been primarily formulated using renewable resources or biodegradable materials such as carbon dioxide,^{12–14} lignocellulose,^{15–17} polyesters,^{18,19} and organosulfur compounds.^{20–22} Although previous studies have predominantly focused on producing high-performance adhesives with scant attention to production scalability, some

reports showcase sustainable adhesives with scalable production capabilities. McNeil et al. have devised synthetic pathways for adhesives sourced from superabsorbent polymer waste, demonstrating significant environmental advantages at large scales, as confirmed by life cycle assessments.²³ Shuai et al. have proposed a scalable approach for manufacturing wood adhesives from lignocellulosic biomass, optimizing the preparation and curing parameters for lignin-based adhesives to ensure cost-effectiveness and scalability.²⁴ Additionally, Wilker et al. have engineered fully biomass-derived adhesives with adhesion strengths comparable to those of conventional

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a) Sustainable adhesive with biodegradability, removability, and scalability



b) Design of sustainable hot-melt adhesives

[Factor 1] Compatibility (heating/cooling state)

- H-bonding between base polymer and rosin

[Factor 2] Wettability (heating state)

- Viscoelasticity of mixture
- Surface energy of mixture

[Factor 3] Crystallization (cooling state)

- Crystallization of adhesive in cooling state
- Adhesion strength adjustment by crystallization behavior

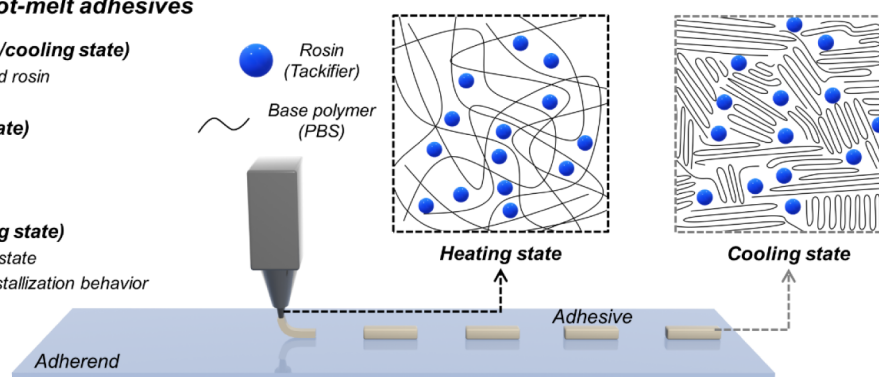


Figure 1. (a) Schematic of a sustainable adhesive exhibiting biodegradability, removability, and scalability. (b) Design strategy for manufacturing sustainable hot-melt adhesives.

epoxy adhesives. Such adhesives are derived from readily available, large-scale production materials such as epoxidized soy oil, malic acid, and tannic acid, with costs comparable to those of conventional epoxy adhesives.²⁵ However, most studies on sustainable adhesives have focused on achieving permanent adhesion rather than removability, hindering their potential for recyclability.


For the production of sustainable adhesive products, both biodegradability and removability are essential. When employing two distinct biodegradable substrates as adherends, the adhesive materials that bind them must provide permanent attachment but degrade after disposal. However, typically, nondegradable or recyclable adherends are used on either side, with removable adhesives being more promising for reusability or recycling features. Traditionally, two types of adhesive removabilities exist. First, adhesives can be engineered to diminish their adhesion strength under specific stimuli such as light^{26–30} and temperature.^{31–33} Although effective, this approach is constrained to industries requiring small adhesive volumes owing to scalability limitations. Second, the adhesion strength can be intentionally reduced to enable removability or repositionability, as in the case of labels, surface protection films, and products such as Post-it notes.¹⁹ While this method only applies in fields requiring lower adhesion strength, it can be produced on a large scale and covers a significant portion of the global adhesive market share (such as the self-adhesive label market, valued at \$53.2 billion in 2023).³⁴

In this study, we devised a novel approach for creating sustainable adhesives, focusing on their biodegradability, scalability, and removability (Figure 1a). Poly(butylene succinate) (PBS), an aliphatic polyester with excellent biodegradability, was selected as the base polymer. To afford the desired adhesive properties, three variants of rosin were tested as tackifiers. Commercially available materials were employed exclusively to ensure scalability. Traditionally, the mixing of hot-melt adhesives has mainly utilized batch mixing methods, which are not continuous. However, twin-screw extrusion enables continuous mixing, making it favorable in terms of scalability. Mixing was facilitated using a twin-screw extruder; this enabled a mass production of a few kilograms and simplified blending while maintaining uniformity. Following adhesive preparation, various factors were analyzed, including compatibility, wettability, and crystallization behavior, all of which are crucial for determining the adhesion strength (Figure 1b). Finally, we identified the optimal conditions for removable adhesion strength and demonstrated the biodegradability of the resulting adhesives. This approach enhances adhesive sustainability and can serve as reference for further advancements in tailoring adhesion strength for diverse applications in future research.

RESULTS AND DISCUSSION

Design Strategy. The development of hot-melt adhesives for labeling and packaging purposes is very promising, given their extensive daily utilization in bonding recyclable, reusable,

a) ■ Typical types of bio-derived tackifiers for hot-melt adhesive

Representative Chemical structure of rosin	Rosin	Rosin D	Rosin ester
	- Type: basic rosin - M_n : 900 g/mol - Acid value: 190 mgKOH/g - Softening point: 83.5 °C	- Type: disproportionated rosin - M_n : 1,000 g/mol - Acid value: 154 mgKOH/g - Softening point: 81 °C	- Type: rosin ester - M_n : 1,800 g/mol - Acid value: 15.4 mgKOH/g - Softening point: 92.5 °C

■ Compatibility between PBS and tackifier

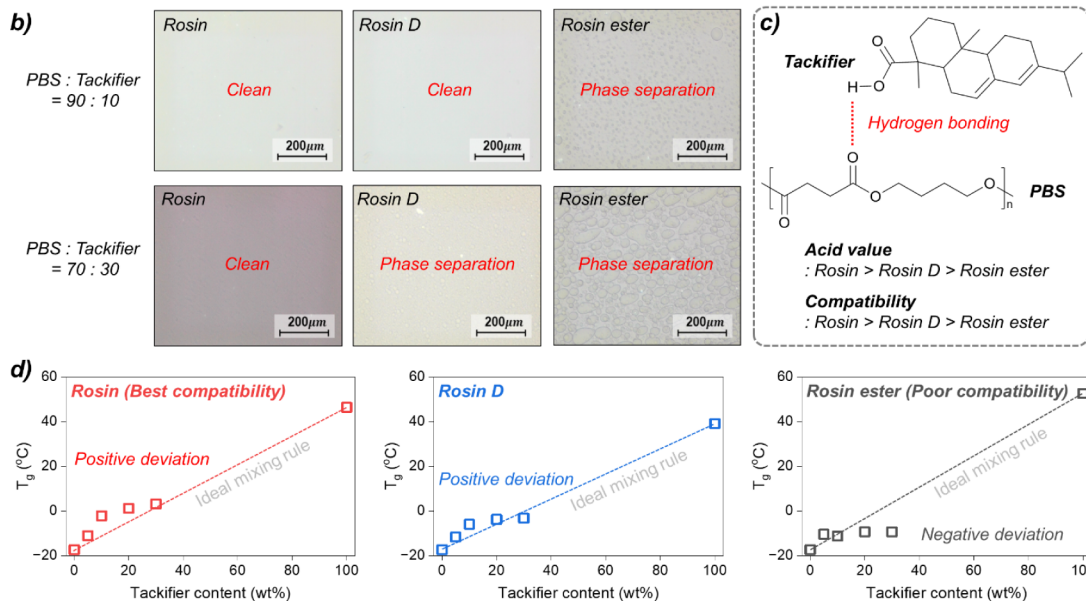


Figure 2. (a) Chemical structures of rosin-based tackifiers for hot-melt adhesives. (b) Polarized optical microscope (POM) images of hot-melt adhesives in a melt state. (c) Schematic of the formation of hydrogen bonding between the tackifier and PBS, enhancing their compatibility. (d) Glass transition temperature (T_g) changes by types and contents of rosin-based tackifiers.

and disposable materials. Hot-melt adhesives typically comprise a base polymer blended with a tackifier; they are applied in a molten state and solidify upon cooling offering adhesion functionality.³⁵

Thermoplastic polymers such as ethylene vinyl acetate and polyolefin (PO) are common base polymers used in hot-melt adhesives,³⁵ however, they lack biodegradability after disposal. To address this, biodegradable hot-melt adhesives require base polymers, such as biodegradable aliphatic polyesters (Table S1).^{36–38} Biodegradable polyester polymers are generally classified into five categories: poly(lactic acid) (PLA), poly(butylene adipate-co-terephthalate) (PBAT), poly(hydroxyalkanoates) (PHAs), poly(ϵ -caprolactone) (PCL), and PBS. However, each of these polymers has its limitations: brittleness (e.g., PLA), petroleum-based source (e.g., PBAT), high cost (e.g., PHAs), and low thermal stability (e.g., PCL).^{39–41} In this study, PBS was selected owing to its biomass origin, melt processability, biodegradability, and commercial availability,^{42–44} endowing both sustainability and biodegradability to the adhesive. Furthermore, it was hypothesized that the inherent warping tendency of semi-crystalline PBS will offer low adhesion sufficient for removability,⁴⁵ with the possibility of adjusting adhesion strength by controlling its crystallization behavior.⁴⁶

Hydrocarbon- or rosin-based tackifiers, are usually added to provide adhesion to thermoplastic polymers. Hydrocarbon tackifiers are predominantly derived from petroleum, whereas rosin-based tackifiers are fully sourced from trees.¹ Hence, rosin-type tackifiers were chosen in this study, including basic rosin (rosin), disproportionated rosin (rosin D), and rosin

ester (Figure 2a and Table S2). These tackifiers are commercially accessible and share similar softening points, thereby ensuring consistent melting and application temperatures for the resulting hot-melt adhesives. The weight ratios between PBS and the tackifiers were varied across different formulations.

Compatibility. In hot-melt adhesive formulations, the compatibility between the base polymer and tackifier significantly affects the adhesion strength. After mixing PBS with the tackifier using a twin-screw extruder, the mixture underwent hot pressing on glass (160 °C, 3 min, 100 gr), followed by immediate morphology characterization in a molten state using a polarized optical microscope (POM, Figures 2b and S1). Phase separation was evident in adhesives containing rosin ester, indicating poor compatibility with PBS. Adhesives with lower amounts of rosin D did not exhibit any phase separation; however, their compatibility deteriorated with increasing rosin D content. Notably, rosin, with the highest acid value among the tested tackifiers, exhibited the best compatibility with PBS, without exhibiting any macroscopic phase separation even at high tackifier loadings. This compatibility was shown to be caused by hydrogen bonding between the carboxylic acid of rosin and the ester bond of PBS. To verify hydrogen bonding between PBS and rosin, the carbonyl peaks were confirmed through Fourier-transform infrared spectroscopy (FT-IR) (Figure S2). The hot-melt adhesive with rosin, a free carbonyl peak by PBS, and a hydrogen-bonded peak by rosin could be observed. It was confirmed that the hydrogen-bonded peak in the hot-melt adhesives had shorter wavelengths than the hydrogen-bonded

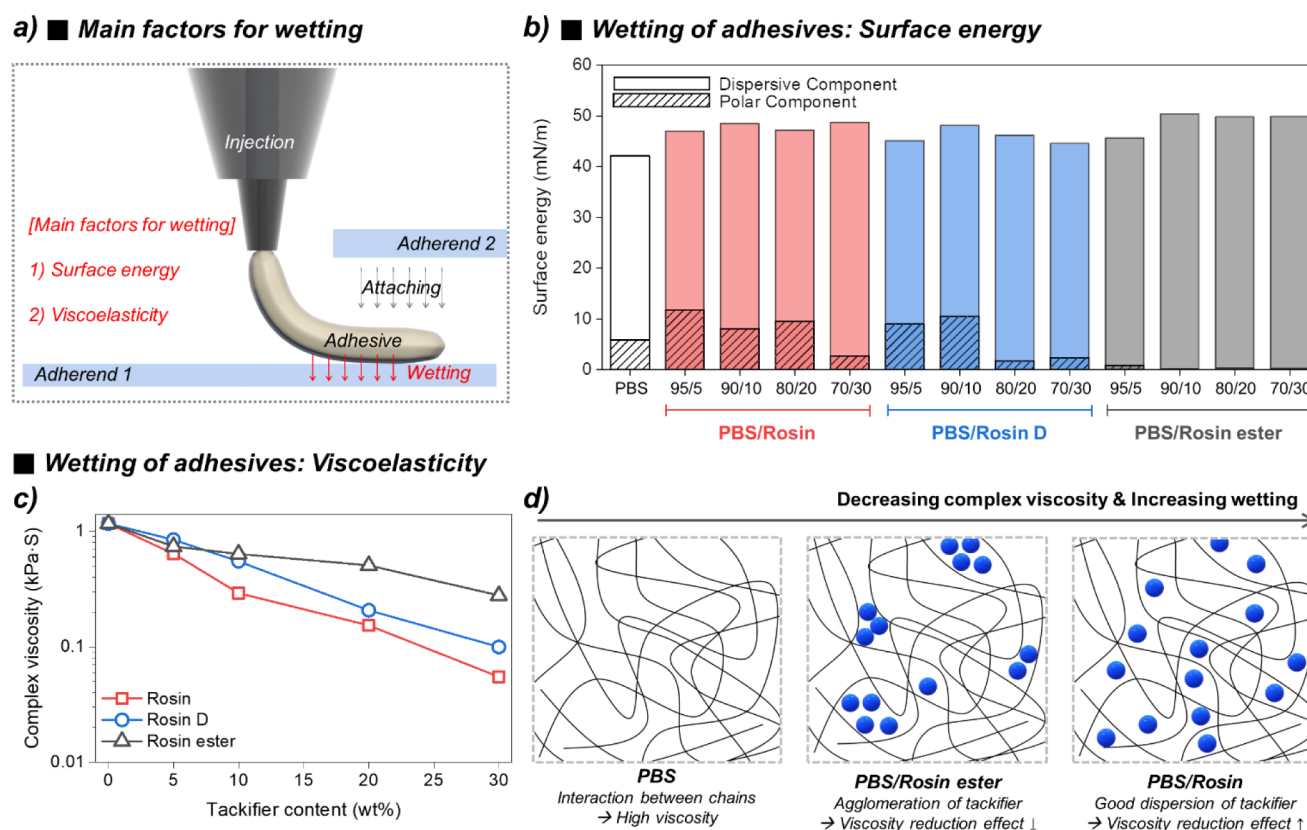


Figure 3. (a) Schematic of the wetting procedure of adhesives. (b) Surface energies and (c) viscoelasticity of the prepared hot-melt adhesives with different types and content of rosin-based tackifiers. (d) Schematic of the relation between viscosity and compatibility.

peak of rosin. Through the carbonyl peak shift, it was indirectly confirmed that hydrogen bonding was formed between PBS and rosin. This trend was similar to rosin D, but was not observed in rosin ester. This exceptional compatibility is possibly due to hydrogen bonding between the tackifier and PBS, which is accelerated by increasing the acid value of the tackifier (Figure 2c).

Furthermore, the compatibility of polymer blends or composites can be assessed by comparing their glass transition temperatures (T_g) with those of different formulations. Generally, excellent compatibility ($\Delta H_{\text{mix}} < 0$) leads to a positive deviation of the composite's T_g from the ideal mixing rule.⁴⁷ Adhesives containing rosin exhibited the highest positive deviation; however, this decreased when 30 wt % of rosin was used, indicating that excess amounts of tackifier saturated compatibility (Figure 2d). Adhesives with a low rosin D content initially showed positive deviation; however, this shifted to negative with increasing tackifier content. Adhesives with rosin ester exhibited negative deviation, indicating poor compatibility with PBS. These findings support the notion that tackifiers with high acid values show superior compatibility with PBS, as previously observed in the POM images.

Wettability. Interfacial adhesion relies heavily on adhesive wettability, as it facilitates intimate contact and enhances the adhesion strength. The wettability of adhesives is predominantly influenced by their surface energies and viscoelastic properties (Figure 3a).^{48,49}

First, the surface energy was assessed using a contact angle analyzer with three standard liquids: distilled water, ethylene glycol, and diiodomethane (Figure 3b). Although the inclusion of the tackifiers marginally increased the surface energy, no

notable disparities were observed. However, the polar component of surface energy notably rose with the addition of rosin or rosin D, attributed to their high acid values. Conversely, at higher concentrations of tackifiers, a significant decrease in the polar component occurred, which can be attributed to tackifier agglomeration induced by hydrogen bonding. Adhesives containing rosin ester exhibited the lowest polar component, possibly due to the tackifier's lower acid value and high agglomeration. A highly polar component can enhance the interfacial adhesion through an increased dipole moment; therefore, it was anticipated that adhesives containing rosin or rosin D would exhibit superior adhesion strength compared to those containing rosin ester.

The viscoelasticity was characterized using a rheometer; complex viscosity was determined under isothermal conditions at varying frequencies. The complex viscosity at 10 Hz (similar to the 100-rpm frequency employed during mixing via a twin-screw extruder) was obtained (Figure 3c) to assess the viscoelasticity under practical conditions. The studied adhesives demonstrated significantly decreasing complex viscosity with increasing tackifier content; this decrease was strongly dependent on the compatibility of the tackifier with PBS (Figure 3d). Adhesives with a high rosin content, exhibiting excellent compatibility with PBS, displayed a sharp decrease in complex viscosity, whereas those with rosin ester exhibited a considerably higher viscosity due to tackifier agglomeration. The difference was more clearly confirmed in the curves of storage modulus and loss modulus (Figure S3). It was considered that rosin with good compatibility could facilitate slip by weakening the intermolecular interaction between polymer chains in PBS. It was assumed that this

Crystallization of hot-melt adhesive

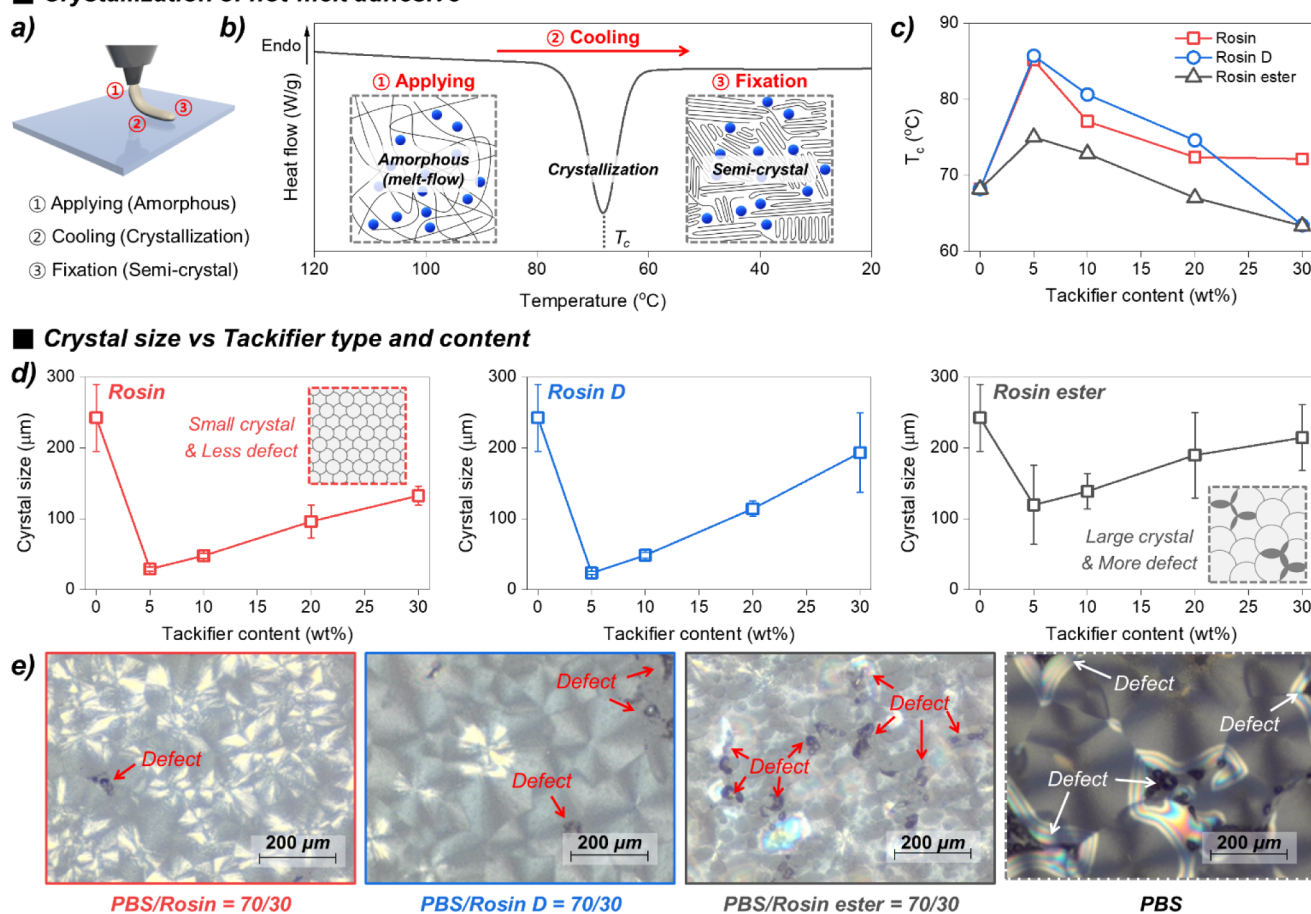


Figure 4. (a) Schematic and (b) heat-flow curve of the bonding process of hot-melt adhesives. (c) Crystallization temperature (T_c) of the prepared hot-melt adhesives. (d) Crystal size with different type and content of tackifiers obtained from POM images (Figures S8–S10) after cooling. (e) POM images with different types of tackifiers (30 wt %). Cooling time was fixed as 110 s.

decreases G' and G'' , which, in turn, increases flowability at low frequency. However, it was confirmed that rosin ester with poor compatibility rather increases G' due to tackifier agglomeration. Based on these viscoelasticity findings, it was anticipated that adhesives containing rosin would exhibit the highest adhesion strength because of their lower viscosity, facilitating intimate adhesive–adherend contact.

Crystallization Behavior. Hot-melt adhesives were initially applied in the molten state and then solidified upon cooling to provide adhesion strength (Figure 4a). During this cooling phase, the adhesives underwent crystallization, transitioning from an amorphous to a semicrystalline structure (Figure 4b). As the surface morphology of an adhesive significantly affects its adhesive properties, understanding its crystallization behavior is crucial.

The two main parameters influencing the crystallization behavior are the crystallization temperature (T_c) and crystal size. First, T_c was determined through a cooling cycle using differential scanning calorimetry (Figures 4c and S4). Incorporation of a small amount of tackifier (5 wt %) resulted in a sharp increase in T_c , indicating rapid solidification at higher temperatures. Although no significant differences were observed in crystal structure and the crystallinity of the prepared adhesives (Figure S5 and Table S3), the addition of tackifiers likely promoted nucleation, thus accelerating crystallization. Hydrogen bonding between polyester and filler

acts as a driving force for the crystallization of the molten polymer during cooling.^{50,51} The carboxylic acid of rosin simultaneously promoted nucleus formation by hydrogen bonding with the ester bond of PBS, which resulted in accelerated crystallization. The nucleating effect by rosin was confirmed by the increase in T_c . On the other hand, the rosin ester could not create hydrogen bonds with PBS, resulting in a lower nucleating effect. Furthermore, it was shown that T_c of the hot-melt adhesives decreased as the concentration of rosin and rosin D increased. It was suggested that the molecules of rosin and rosin D form microscopic aggregation as the rosin content increases, since aggregation of fillers reduces the nucleating effect.⁵¹ The crystal growth was examined from POM images obtained at different cooling times. Following a pattern akin to the Avrami model,⁵² circular crystal growth was initiated from randomly dispersed nucleation sites, with spherulite growth completed within 2 min (Figures S7–S10). When 5 wt % rosin was used as the tackifier, the crystal size in the final morphology after cooling decreased significantly (Figure 4d), which was attributed to the rapid crystallization induced by the high compatibility. Conversely, an increase in the rosin content led to enlargement of the crystal size due to slowed crystallization from the reduced compatibility. Adhesives containing rosin D showed similar trends but displayed slightly larger crystal sizes due to its lower compatibility with PBS compared to rosin. Adhesives

■ Peel strength of hot-melt adhesives

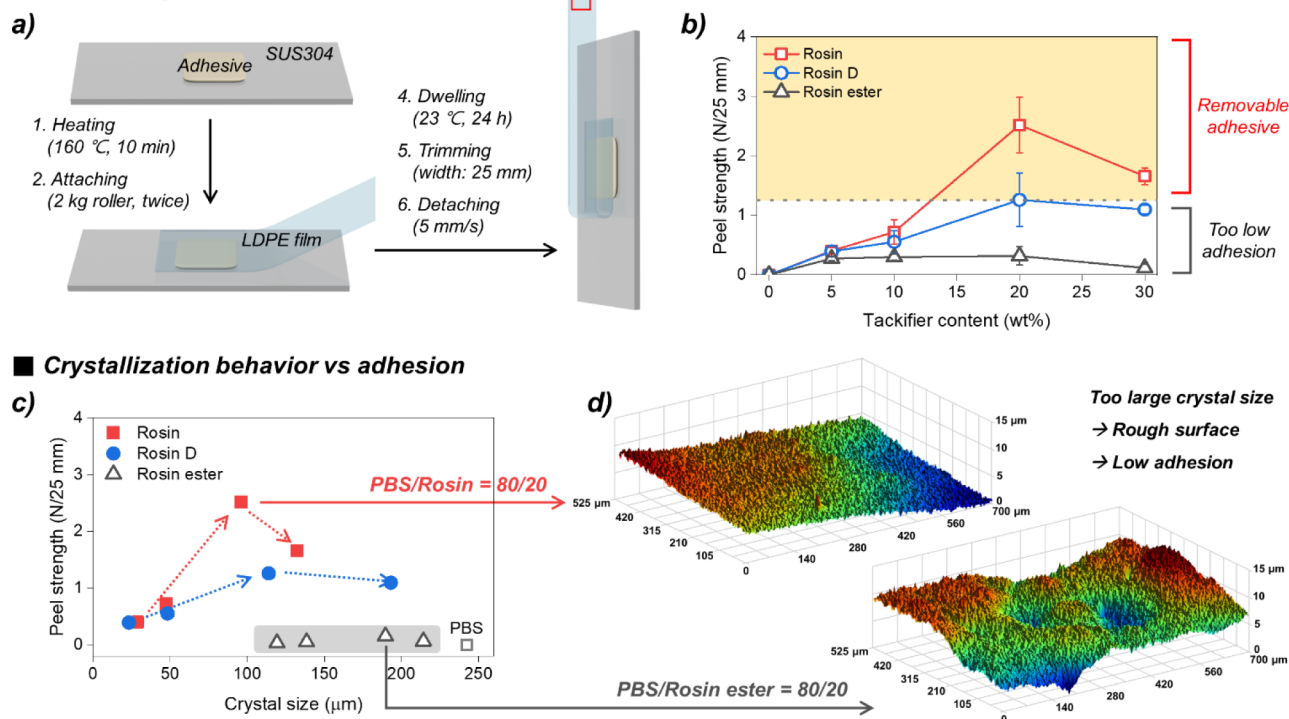


Figure 5. (a) Schematic of the peel test on hot-melt adhesives. (b) Peel strength of the prepared hot-melt adhesives. (c) Relation between crystal size and peel strength of the prepared hot-melt adhesives. (d) 3D surface morphology images of hot-melt adhesives containing rosin or rosin ester after peeling, obtained via three-dimensional laser confocal microscopy.

incorporating rosin ester exhibited the largest crystal sizes owing to poor compatibility with PBS. Moreover, numerous defects were observed in the POM images (Figure 4e), possibly attributed to the local absence of birefringence due to the disordering of polymer structures.⁵³ Strong birefringence occurred when the defects were generated at the interface between the hot-melt adhesives and the glass in the last moment when the spherulites collided (Video S1). The poor compatibility of rosin ester likely contributed to an increased average and deviation of crystal size, generating numerous defects. It was anticipated that adhesives containing rosin, exhibiting fewer defects in the POM images, would demonstrate the highest adhesion strength, supporting the trends derived from the wettability results.

Removable Adhesion. To assess the adhesion strengths of the prepared hot-melt adhesives, we conducted a 180° peel test using corona-treated low-density polyethylene (LDPE), a common food packaging material (Figure 5a). The adhesives were placed between a SUS304 substrate and LDPE film and were subjected to heating (160 °C, 10 min) and pressure (2 kg roller applied twice). No additional curing process was performed because reactive chemicals (e.g., cross-linking agent, chain extender, etc.) were not blended. After 1 d at room temperature (23 °C) and trimming, the trimmed specimens were peeled off at a specific angle (180°) and speed (5 mm/s) using a texture analyzer (TA.XT plus C, Stable Micro Systems Ltd.).

Pure PBS without the tackifier exhibited no adhesion due to significant defects; however, the addition of the tackifier improved its adhesion strength (Figure 5b). Adhesives containing rosin exhibited the highest adhesion strength, possibly because of their superior wettability and reduced crystal defects. It was noteworthy that adhesion strength

decreased at 30 wt % of rosin. Compared to 20 wt % of rosin, it showed no significant variation in roughness and decreased viscosity and G' . The diminished adhesion strength at 30 wt % of rosin may result from decreased polar component due to saturation in compatibility with PBS and rosin. The decrease in the polar component was attributed to the increased hydrophobic property or hydrophenanthrene structure in rosin, resulting from the agglomeration of extra rosin. Because the adhesives are thermoplastic without chemical reaction to the adherend, the adhesion strengths depended on secondary bonds rather than primary bonds. Therefore, the decrease in the polar component was shown to diminish hydrogen bonding and dipole–dipole interaction, resulting in a drop in adhesion strength at 30 wt % of rosin. Importantly, adhesives with 20 or 30 wt % rosin exhibited sufficient adhesion strengths for use as removable or repositionable adhesives (approximately 1.25–4 N/25 mm).^{19,54} Compared with commercial removable adhesives and PO-based hot-melt adhesives, the prepared hot-melt adhesives in the study exhibited sufficient removable bonding strength (Figure S11). The commercial removable adhesives also showed adequate adhesion strength and debonded without any specific stimulus. On the other hand, the PO-based hot-melt adhesives were not suitable as removable adhesives because they exhibited excessively strong adhesion and cohesive failure. Therefore, we determined that the hot-melt adhesives with 20 or 30 wt % of rosin were suitable as removable adhesives. Adhesives with rosin D showed similar trends but lower adhesion strength due to reduced compatibility with PBS. Adhesives containing rosin ester exhibited the lowest adhesion strength owing to their poor wettability and numerous crystal defects.

Biodegradability of hot-melt adhesive

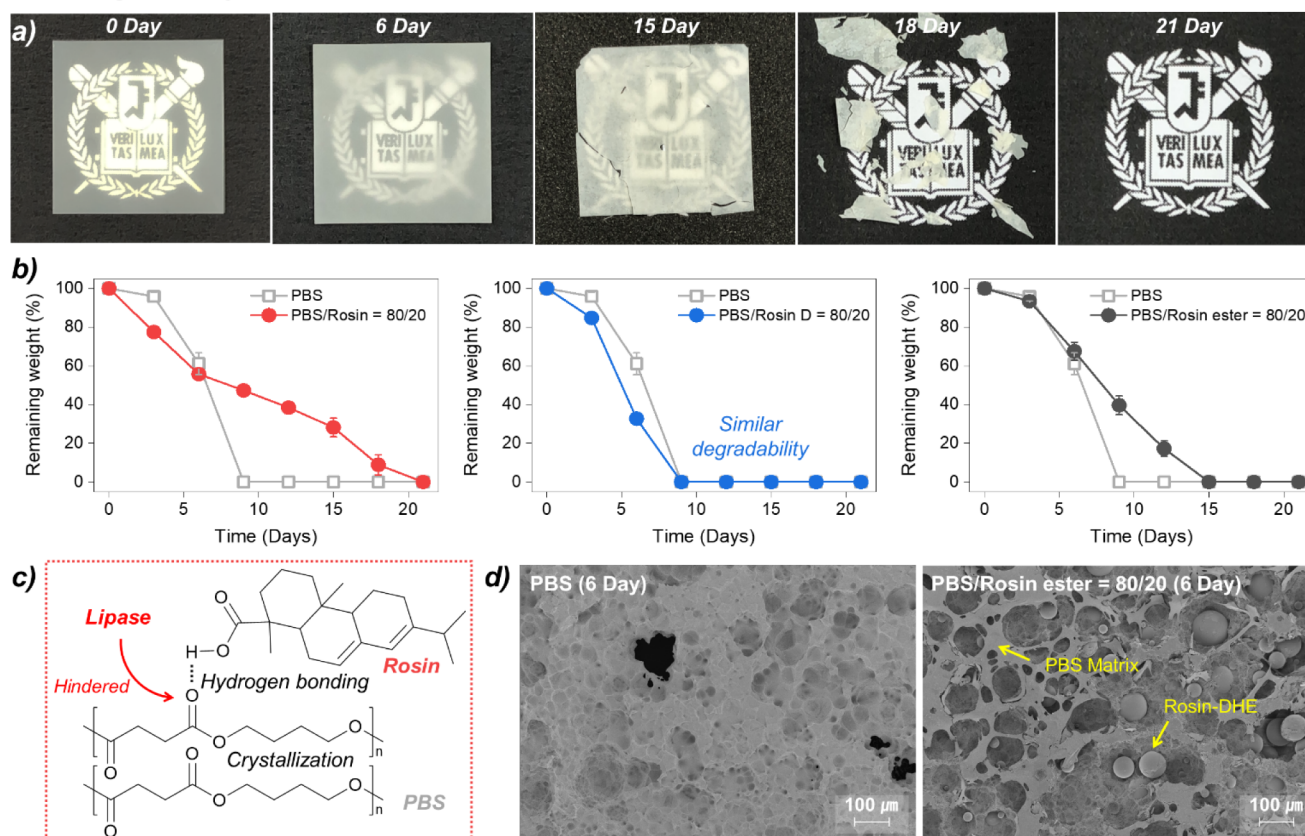


Figure 6. (a) Images of degraded hot-melt adhesives containing 20 wt % rosin at different degradation times. (b) Weight remaining against degradation time for different types of tackifiers. (c) Schematic of the slow degradation of adhesives containing rosin. (d) Scanning electron microscope images of degraded PBS and PBS containing rosin ester.

It was hypothesized that the adhesion strength correlates strongly with the crystallization behavior; therefore, the peel strength was plotted against crystal size (Figure 5c). The adhesion strength of hot-melt adhesives containing rosin increased significantly with larger crystal sizes, possibly because of the slower crystallization rates. Slower solidification provides sufficient time for the molten adhesives to adhere well to the adherend, resulting in strong adhesion. However, excessively large crystal sizes can lead to numerous crystal defects, thereby reducing the adhesion strength. Adhesives with rosin D exhibited similar trends but lower adhesion strength owing to differences in compatibility between PBS and the tackifier. Adhesives containing rosin ester showed low adhesion strength regardless of their crystal size, possibly due to poor compatibility, high complex viscosity, and low polar component surface energy. Additionally, numerous crystal defects may increase the adhesive surface roughness, thereby significantly reducing the adhesion strength. The three-dimensional surface morphology via three-dimensional laser confocal microscopy confirmed that rosin-based adhesives were relatively flat, whereas rosin ester-based adhesives had very rough surfaces (Figure 5d and Table S4). Since interfacial failure was observed in all hot-melt adhesives on adherends after peel tests, we concluded that the high roughness was due to sporadically small defects that occurred after colliding between spherulites.

Biodegradability. Biodegradable polymers deteriorate through bulk erosion and surface erosion mechanisms when decomposition occurs. In bulk erosion, bonds (e.g., ester

bonds) in biodegradable polymers are randomly cleaved by water, lowering the molecular weight. Surface erosion occurs when the surface is eroded by lipase or microorganisms.⁵⁵ In general, PBS is susceptible to hydrolysis and undergoes rapid bulk erosion by water.⁵⁶ The biodegradability of the prepared hot-melt adhesives was evaluated through enzymatic degradation tests using lipase, a well-known enzyme accelerating the degradation of PBS.⁴² A phosphate buffer solution with a pH of 6.0 (14.85 mL) was mixed with lipase (0.15 mL), and adhesive specimens with specific dimensions (length: 2.5 cm, width: 2.5 cm, thickness: 0.1 mm) were immersed in the solution. The mixture was then maintained at 50 °C with continuous agitation, and the weight of the adhesive was measured after gently wiping the solution from the surface.

The adhesive formulation containing 20 wt % rosin exhibited sufficient adhesion strength to be utilized as a removable adhesive and demonstrated satisfactory biodegradability, being completely degraded by lipase within 21 d (Figure 6a). Such a rapid decomposition rate has not been observed in previous sustainable hot-melt adhesive studies (Table S1). The prepared adhesives exhibited slightly slower degradation than the pristine PBS (Figure 6b) because of hindrance in lipase access caused by the well-dispersed and hydrogen-bonded tackifier (Figure 6c).⁴⁰ However, degradation rate of the prepared adhesive was comparable to that of other biodegradable polymers.⁴³ Adhesives containing rosin D showed a degradation behavior similar to pristine PBS, while the incorporation of rosin ester resulted in a lower degradation rate. This could be attributed to the poor compatibility of rosin

ester, which hindered access to lipase via the large-scaled phase separation between PBS and the tackifier (Figure 6d).⁴⁰

CONCLUSIONS

We present an innovative strategy for manufacturing sustainable adhesives exhibiting biodegradability, removability, and scalability. To ensure biodegradability and scalability, we prepared the hot-melt adhesives using rosin-based tackifiers and PBS, both readily available commercially. By employing three types of tackifiers, basic rosin (rosin), disproportionated rosin (rosin D), and rosin ester, we determined that rosin exhibited superior compatibility and wettability due to its high acid value. The use of rosin accelerated crystallization and minimized the crystal size, thereby reducing the occurrence of crystal defects. Furthermore, we observed that slower crystallization enhanced the adhesion strength, affording sufficient time for wetting onto the adherend. However, excessive crystal sizes compromised the peel strength owing to crystal defects. The hot-melt adhesive containing 20 wt % rosin, an optimal composition, exhibited satisfactory adhesion strength (2.5 N/25 mm) suitable for use as a removable or repositionable adhesive (1.25 N/25 mm). Moreover, it demonstrated sufficient biodegradability and completely decomposed within 21 d. Our findings offer a practical approach for enhancing the sustainability of adhesives, with the potential for further refinement by adjusting the adhesion strength across a broader spectrum in future endeavors.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c03234>.

Table S1: references of sustainable hot-melt adhesives; Table S2: gel permeation chromatography (YL9100 HPLC, YL Instrument) results for tackifiers; Table S3: thermal properties of hot-melt adhesives, obtained by differential scanning calorimetry; Table S4: surface roughness of hot-melt adhesives, obtained by three-dimensional (3D) laser confocal microscope; Figure S1: polarized optical microscope (POM) images of hot-melt adhesives with different types and contents of rosin-based tackifiers; Figure S2: (a) chemical structure of poly(butylene succinate) (PBS) and tackifier (rosin) and FT-IR results of hot-melt adhesives with different rosin types and contents: (b) rosin, (c) rosin D, and (d) rosin ester; Figure S3: frequency-dependent complex viscosity (η^*) of hot-melt adhesives containing (a) rosin, (b) rosin D, or (c) rosin ester as a tackifier and frequency-dependent loss factor (G''/G') of hot-melt adhesives containing (d) rosin, (e) rosin D, or (f) rosin ester as a tackifier; Figure S4: heat flow curves of the hot-melt adhesives containing rosin, which was assessed by differential scanning calorimetry; Figure S5: X-ray diffraction (XRD) spectra of hot-melt adhesives containing rosin or rosin ester; Figure S6: heat flow curves of the hot-melt adhesives containing rosin by DSC; Figure S7: average of crystal size of hot-melt adhesives as a function of cooling time; Figure S8: POM images of hot-melt adhesives containing rosin as a function of cooling time and blending ratio; Figure S9: POM images of hot-melt adhesives containing rosin D as a function of cooling time and blending ratio; Figure

S10: POM images of hot-melt adhesives containing rosin ester as a function of cooling time and blending ratio; Figure S11: (a) peel strength of PBS/rosin hot-melt adhesives compared to commercial adhesives and (b) photos of the failure mode of hot-melt adhesives following the peel test; Figure S12: scanning electron microscope images of degraded PBS with different degradation time; Figure S13: scanning electron microscope images of degraded hot-melt adhesives containing rosin with different degradation time; Figure S14: scanning electron microscope images of degraded hot-melt adhesives containing rosin ester with different degradation time (PDF)

Video S1: crystallization behavior of the prepared hot-melt adhesives (MP4)

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Author Contributions

K.-H.R. contributed to conceptualization, investigation, writing, original draft. J.-H.C. contributed to validation. T.-H.L. contributed to conceptualization. H.K. contributed to methodology. G.-Y.H. contributed to methodology. J.-H.B. contributed to writing-review and editing, supervision, and conceptu-

alization. H.-J.K. contributed to project administration and funding acquisition.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

PBS Poly(butylene succinate)
POM polarized optical microscopy
LDPE low-density polyethylene

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