# Adhesive Properties of Eco-Friendly Hot Melt Adhesive Based on Poly(butylene adipate-co-terephthalate) and Rosin Maleic Resin

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As environmental problems increase, disposable products are being replaced and recommended with materials with a low environmental load when it discarded. So the demand for bioplastics for building a sustainable society is increasing. This study focuses mainly on the applicability of biodegradable plastics and rosin maleic resin (RMR, DX-250) blends with potential use in eco-friendly hot-melt adhesives (HMA). Poly (butylene adipate-co-terephthalate) (PBAT), which has high dimensional stability owing to low crystallinity, is used as the main polymer of the HMA. And rosin maleic resin, which is effective for increasing adhesive properties and compatibility as a tackifier. The HMA based on PBAT and RMR blends are prepared via melt-blend extrusion. Compatibility and wettability are increased under the influence of RMR, and adhesion properties are improved, compared to that of

PBAT. In addition, as confirmed polarizing microscope (POM), the addition of RMR leads to a decrease in crystallinity, which can be expected to be effective for biodegradation. This result PBAT/RMR 7/3 blend significantly enhances the adhesion strength of PBAT from 1.8 to 7.3 MPa. Therefore, PBAT with the blends containing 30 wt.% of RMR has considerable potential application in the HMA field.

# 1. Introduction

Plastic utilization has profoundly influenced daily life and industrial plastics, attributed to their convenience, facile processing, exceptional longevity, and affordability. Nevertheless, the very

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convenience of plastics has precipitated their indiscriminate usage, resulting in a dramatic escalation in global plastic production, which has increased over 200 times from 1950 to 2015.<sup>[1]</sup> This widespread use of plastic has become a major factor in environmental degradation and poses a direct threat to the living organisms.<sup>[2]</sup> Despite these concerns, the trend toward increasing reliance on disposable products persists. In response, there is a growing number of regulations surrounding petroleum-based plastic. At the same time, there is increasing interest in bio-based plastics as a sustainable alternative.<sup>[3,4]</sup> Bioplastics are mainly divided into two categories: 1) biodegradable plastics, which include poly(lactic acid) (PLA), poly(hydroxyalkanoates) (PHA), and poly(butylene adipate-coterephthalate) (PBAT), and 2) biomass plastics, which contain a certain amount of biomass, such as bio-polyethylene (Bio-PE), bio-polypropylene (Bio-PP), and biopoly(ethylene terephthalate) (Bio-PET).<sup>[5-9]</sup>

Biodegradable plastics are highly regarded for their ability to decompose safely, making disposal much safer. Among different applications, it is the packaging sector that has the highest demand.<sup>[10]</sup> Pertinently, petrochemical-based products serve as adhesives in packaging materials. Although these adhesives constitute only 3% of the packaging composition, they are indispensable in virtually all packaging applications.<sup>[11]</sup>

Adhesives are classified as solvent-borne, waterborne, hotmelt, and UV-curing adhesives. In the past 25 years, HMA has seen a significant increase in use. This is mainly due to efforts to reduce the environmental and health risks associated with solvent use and the release of volatile organic compounds (VOCs).<sup>[12-17]</sup> Characteristically, HMAs are solvent-free thermoplastics, exhibiting a solid state at lower temperatures and transforming into a low-viscosity fluid at elevated temperatures, with rapid solidification upon cooling. HMA is typically composed of three or four components. The base polymer, which makes up  $\approx$  33.3% of the composition, helps to enhance mechanical properties. Tackifiers, which also make up roughly 33%, are important in regulating adhesion characteristics. Waxes, which make up another 33%, are used to adjust melt viscosity and setting time. Additionally, selective additives are included to prevent degradation resulting from thermal and photonic exposure, with

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antioxidants and light stabilizers being common additives.<sup>[12]</sup> Although HMAs are used in various domains, their inability to biodegrade fully upon disposal, even when attached to biodegradable substrates, is a significant limitation of petroleum-based HMAs. The adhesive industry has been undergoing a shift toward developing eco-friendly adhesives due to the increasing societal interest in environmental conservation. This has led to the use of natural materials in the production of these adhesives, which has significantly reduced their environmental impact. Recently, as interest in the environment has increased in society, the focus of the adhesive field has also shifted to eco-friendly adhesives with a low environmental load.[18-22] The production of these environmental adhesives necessitates the utilization of natural materials. Biodegradable plastics offer significant environmental benefits, including the reduction of pollution and the capacity for biodegradation. Nonetheless, when compared to petroleum-based plastics, biodegradable plastics have significant drawbacks. They may decompose during distribution and have inferior physical properties, including brittleness and ductility. Therefore, to compensate for the physical property limitations and to achieve desirable biodegradability, aliphatic-aromatic co-polyesters have been studied, which are synthesized by aliphatic and aromatic units.<sup>[23,24]</sup> Among the aliphatic-aromatic co-polyesters, PBAT has been the most appropriate combination for achieving biodegradability due to its aliphatic unit and outstanding physical properties due to its aromatic unit.[25,26] The application of PBAT to HMA is distinguished by low crystallinity and less specific volume contraction<sup>[27,28]</sup> compared to other biodegradable polymers. In addition, it provides low contractility and excellent dimensional stability for maintaining adhesion. Adhesives need to maintain their volume and adhere securely to surfaces. However, the crystallization can cause shrinkage and affect dimensional accuracy by rearranging the chains. To avoid these issues, it is important to use adhesives that minimize specific volume contraction. This results in increased contact area between the substrate and the adhesive, making it capable of bearing more load until it reaches it fracture strength.<sup>[29-31]</sup>

Based on these characteristics, PBAT is considered to be worth researching as an HMA product when blended with other materials. Rosin is a natural resin produced by distilling pine resin. It acts as a tackifier and is a renewable and biodegradable polymerizable monomer, making it useful in various adhesive applications, including coatings and binders. The complex structure of rosin has been recognized as a potentially crucial renewable resource. However, its unsaturation could cause darkening and reduced adhesive quality when exposed to oxygen. Therefore, additional chemical treatments are used to improve the stability of rosin and make it more durable. Rosin has two reactive groups: a double bond and a carboxyl group. These groups can be modified to alter their properties. The corresponding reaction site is modified in various ways to produce a highly durable material.<sup>[32–34]</sup> One of the most common modifications to rosin is through the Diels-Alder reaction with maleic anhydride, which produces derivatives with three carboxylic acid groups.<sup>[35]</sup> This is achieved by hydrating maleic anhydride molecules to form a dicarboxyl acid functional group. The modification increases the acidity of the rosin, thereby enhancing its adhesive properties and compatibility with other substances.[36-39]

This study aims to enhance the processability of hot-melt adhesives made of biodegradable resin. To achieve this, we are integrating materials that possess desirable properties and do not have a significant impact on the environment. We used PBAT and RMR to create a fully bio-based HMA that exhibits efficient processing at low temperature and maintains a low viscosity. Our study evaluated the viscosity reduction due to the RM content to assess processability. We also examined the adhesive strength and tensile strength of the PBAT/RMR blends. An analysis of the crystalline properties of the blends facilitated predictions regarding their degradability. As a result, the PBAT/RMR blends are a promising candidate for eco-friendly HMAs, and they represent a sustainable alternative to traditional petroleum-based HMAs.

## 2. Results and Discussion

#### 2.1. Compatibility of PBAT/RM Blends

Figure 1 shows the melting Figure 1a and cooling curves Figure 1b,c of the PBAT, RMR, and PBAT/RMR blends. DSC thermal data for melting temperature (T<sub>m</sub>), crystallization temperature  $(T_c)$ , and glass transition temperature  $(T_g)$ . The melting curves in Figure 1a of the PBAT, PBAT/RMR blends, and RMR showed that  $T_{\rm m}$  and  $\Delta H_{\rm m}$  decreased as the RMR content increased. This phenomenon generally occurs when a blend system of crystalline polymer/amorphous polymer or crystalline polymer/crystalline polymer is compatible with a decrease in melting temperature.<sup>[40]</sup> An increase in RMR content resulted in a cold crystalline peak, indicating that crystal formation of PBAT became more difficult. This suggests that the PBAT blends gradually turned amorphous with an increase in RMR content. It was observed that there was only one crystallization peak for all blend ratios. The cooling curve demonstrated that an increase in RMR content resulted in a decrease in both the crystallization temperature (T<sub>c</sub>) and heat of crystallization ( $\Delta$ H<sub>c</sub>) of the spherical crystals decreased. Meanwhile, it was confirmed that the cold crystallization peak, which is a characteristic of amorphous polymers, appeared in the 7/3 blend (Figure 1c). Cold crystallization occurs when a polymer is cooled in a disordered state without crystallizing. At temperatures above the T<sub>a</sub>, the crystalline segments slowly return to their original structured arrangement. Additionally, with the increased RMR blends, it was evident that the amorphous characteristics were accentuated, making it challenging to observed the T<sub>c</sub>. These results imply that the  $T_c$  and  $H_c$  of the blend, as compared by composition in Table 1, confirm an enhanced mutual dilution effect due to the rosin.<sup>[41]</sup> As the amorphous rosin content increases, crystallization becomes difficult, and the mutual dilution between the two polymers inhibits the spherulite growth rate and crystallinity.

In the cooling curve, PBAT/RMR 7/3 and 6/4 blends, there are no obvious crystallinity points observed. The crystallinity tends to decrease gradually owing to the influence of rosin, which means that the PBAT/RMR blends became amorphous.<sup>[42]</sup> In general, the adhesion of the main chain interface is closely related to the morphology of the contacted polymer. The amorphous main chain, which has relatively high flexibility of the main chains,

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**Figure 1.** DSC Thermograms (a), (b), and (c) for neat PBAT, RMR and its blends with PBAT/RMR blends during heating and cooling ramps for 10 °C min<sup>-1</sup> heating rate. d) observed  $T_g$  and calculated  $T_g$  from Fox equation.

easily adheres to the interface compared to the crystalline main chain. The HMA blends used in this study, the crystallinity decreased as the RMR content increased, and the amorphous region was relatively larger. These results suggest that this phenomenon may affect adhesion increase.<sup>[43,44]</sup>  $T_{\alpha}$  of the polymers are important parameters for industrial processing and the miscibility of the blends.<sup>[45]</sup> The glass transition temperature  $(T_{\alpha})$  is shown in Figure 1c,d. This study confirmed that the T<sub>g</sub> shifted from -30 to -7.4 °C, with a relatively high T<sub>g</sub> as the RMR content of the PBAT/RMR blends increased for each composition. This is almost in agreement with the theoretical value obtained by Fox Equation (1).<sup>[46–48]</sup> It can be seen that the blends behave as ideal mixtures, with no significant phase separation or specific interactions beyond those described by the equation. Moreover, molecular chains of the blends, which limits the ability of the free movement of polymer chains.<sup>[49]</sup>

 Table 1. Thermal properties of the PBAT, PBAT/RMR blends, and RMR obtained from DSC experiments.

Content	T <sub>m</sub> [°C]	T <sub>c</sub> [°C]	T <sub>g</sub> [°C]	$\Delta H_m [J g^{-1}]$	$\Delta H_{c} [J g^{-1}]$
10/0	130.5	87.4	-31.0	12.9	14.1
9/1	123.9	80.1	-21.9	13.7	15.3
8/2	119.0	69.4	-18.2	13.5	15.2
7/3	110.8	52.7	-7.4	9.7	4.2
6/4	109.5	-	-2.2	7.9	-
0/10	-	-	60.1	-	-

### 2.2. Wetting Properties of PBAT/RM Blends

#### 2.2.1. Rheological Properties of PBAT/RM Blends

The wettability of HMA affects the adhesion properties, which influences the wetting or spreading process. The spreading properties of HMA blends were evaluated based on rheological properties (Figure 2a). Figure 2b,c shows the changes in the complex viscosity and storage modulus according to the frequency change at 160 °C. Most polymers show shear thinning behavior with increasing frequency.<sup>[50,51]</sup> Complex viscosities (Figure 2a) of pristine PBAT also showed this phenomenon as the frequency increased.<sup>[52,53]</sup> Conversely, blended composites with the addition of low molecular weight rosin exhibit Newtonian fluid behavior, having a nearly constant complex viscosity at oscillation frequencies <100 rad s<sup>-1</sup>. Moreover, in 7/3 and 6/4 blends, as the content of RMR increases in PBAT/RMR blends, the storage modulus (G') slope increases from low to high frequency.<sup>[54,55]</sup> This behavior can be attributed to the inversion from a PBAT matrix with RMR inclusion to an RMR matrix with PBAT domains, leading to a more rigid and interconnected structure. Consequently, the blend transitions from a more viscoelastic behavior at low frequencies to a glassy behavior at high frequencies due to the dominance of the rigid RMR matrix. Meanwhile, blended composites with the addition of low molecular weight rosin exhibit Newtonian fluid behavior, having a nearly constant complex viscosity at oscillation frequencies <100 rad s<sup>-1</sup>. This behavior shows that the molecular weight of the majority of rosin constituents was not sufficiently high to cause shear thinning behavior. The



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Figure 2. a) schematic diagram of different spreading drop behavior of HMA. Plots of the complex viscosity b) and storage modulus c) of various blends at 160 °C as a function of the shear rate obtained from rheometer.

decrease in complex viscosity is attributed to the faster relaxation of the molecules owing to the interaction between PBAT and RMR. The rosin segment can be softened by PBAT, and these results indicate that the softening effect of rosin becomes more evident when the rosin content is higher. The change in storage modulus is shown in Figure 2b. When the frequency was low, the storage moduli of the 8/2, 7/3, and 6/4 HMA were slightly higher than that of the 9/1. However, in the high-frequency section, rosin ensured that the storage modulus decreased as the RMR content increased. Based on these results, an increase in the RMR content reduces the complex viscosity and endows high spreadability to the PBAT blends.

#### 2.2.2. Determination of Blends Surface Energy

The change in hydrophobicity of the PBAT/RMR blends was observed through contact angle and FT-IR in **Figure 3**. PBAT exhibits hydrophobicity owing to its non-polar parts of polyester chain.<sup>[56–59]</sup> Rosin is not hydrophilic, however, by introducing hydrophilic moieties, it becomes hydrophilic.<sup>[60,61]</sup> The change in hydrophobicity of the hot-melt blended RMR with hydrophilic moieties on PBAT was observed through contact angle measurements (Figure 3a and **Table 2**). When a polymer with less specific volume contraction is used, it can increase the contact area between the substrate surface and the adhesive. This results in



Figure 3. a) Contact angle measured on various samples using water and diiodomethane drops, a), a') PBAT, b), b') 9/1, c), c') 8/2, d), d') 7/3, and e, e') 6/4. Droplet images are observed for each sample. b) FT-IR spectra of PBAT and PBAT/RMR and c) schematic diagram of the PBAT/RMR blends.

Table 2. Contact angles of water and diiodomethane and surface energies of PBAT, PBAT/RMR blends, and RMR.

Content	Water [°]	Diiodomethane [°]	Surface Energy [Nm m <sup>-1</sup> ]
10/0	77.1	34.0	44.5
9/1	72.8	31.9	46.6
8/2	71.1	23.3	49.8
7/3	70.3	22.1	50.3
6/4	75.3	33.8	45.1
0/10	74.3	26.2	47.9

an increase in the load held to the point of the fracture strength of the adhesive, while causing the change in the contact angle. However, small differences in the contact angle can impact the adhesion properties. In PBAT/RMR blends, the contact angle increases with hydrophobic moieties, whereas it decreases with hydrophilic moieties. As the content of RMR with hydrophilic moieties in PBAT with hydrophobic properties increased, the hydrophobicity of the PBAT/RMR blends slightly decreased, resulting in the water contact angles from a) 77.1° PBAT/RMR blends b) 71.6°, c) 71.1°, and d) 70.3°. However, in the 6/4 blend with high rosin content, it was confirmed that the contact angle increased to e) 75.3°. This result is expected to increase the contribution of polarity and surface tension. The same behavior was also observed in the case of diiodomethane, a wetting liquid with high surface tension; the contact angle on the solid surface tends to be smaller from a') 34.0° to d') 22.1. Similarly with the water

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contact angle results, in the 6/4 blend, the contact angle increased to e') 33.8°. It is expected that the effect of the surface polar groups is greater than that of the dispersive force. The contact angle change, according to the amount of rosin added to water with a large specific component, is larger than that of diiodomethane, which has a large dispersive component. The surface free energy of the blends increased with the rosin content but showed a tendency to decrease when rosin was added at 30 wt.% or more and showed the highest value at 7/3 blend. The PBAT and PBAT/RMR blends are presented in the FT-IR spectra (Figure 3b) and schematic diagram (Figure 3c). In the PBAT/RMR blend spectra, the hydroxyl peak appeared at 2924 cm<sup>-1</sup>, corresponding to the carboxylic acid in RMR. Additionally, two carbonyl peaks were observed at 1850 and 1778 cm<sup>-1</sup>, which were derived from the carbonyl group of maleic anhydride. The strength of adhesion is affected by wettability, which is improved when the adhesive can spread better on the surface and form a stronger bond. When a large amount of RMR is added to the PBAT blends, the contribution of polarity increases<sup>[58,62]</sup> due to the hydrophilic functional group of RMR.<sup>[63]</sup> The relatively hydrophilic properties of RMR helped enhance the wettability of PBAT/RMR blends.

#### 2.3. Mechanical Properties of PBAT/Rosin Blends

#### 2.3.1. Lap Shear Strength

The blends were prepared by RMR as a tackifier to compare the adhesion properties (**Figure 4**). As shown in Figure 4a, ethylene



Figure 4. a) Shear strength and fracture images of HMA blends, b) schematic representation of lap shear test, failure mode, and c) schematic image of the factors affecting tackifier improvement in adhesion of polymer matrix.

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Figure 5. a) Stress-strain curve of the tensile test on the dogbone samples for the PBAT and PBAT/RMR blends, b) magnified tensile stress-strain plot shown in figure (a). and c) schematic of deformation process of PBAT and PBAT/RMR blends.

Vinyl Acetate (EVA) HMA exhibited a shear strength of 3.9 MPa. However, upon incorporating RMR in the blends, it was determined that the shear strength of all blends was higher than that of EVA. The composition of 30 wt.% of the total RMR content increased shear strength to 7.3 MPa. However, when the RMR composition was increased to 40 wt.%, the shear strength decreased to 6.8 MPa. As previously mentioned, the introduction of RMR caused the stiffening effect, which was reflected in the T<sub>o</sub> result from DSC. As expected, the molecular rigidity of the blends increased, resulting in a molecular chain stiffening similar to the 6/4 blend. This led to decrease in adhesion strength.<sup>[64]</sup> Consequently, PBAT/RMR blends changed the failure mode from adhesive failure to cohesive failure as shown in Figure 4a. Tackifier into the matrices of HMAs improvements in their adhesion performance (Figure 4c). When tackifier was added to a polymer matrix, they strongly interact with the polymer chains, leading to a more rigid network. This interaction can restrict the mobility of the polymer chains, making it more difficult for them to move. As a result, the  $T_{a}$  increases because the polymer requires more thermal energy to reach the same level of mobility. Moreover, tackifiers enhance the uniformity of the polymer matrix or the more effective distribution of stress throughout the material. Thus, the spreadability observed in the PBAT/RMR blends can be attributed to their rheological properties. When rosin molecules enter the PBAT molecular chains, the viscosity decreases, which increases the wettability to the substrate and enhances adhesion in the overall blends.

#### 2.3.2. Tensile Properties of PBAT/Rosin Blends

The mechanical properties of the PBAT blends were confirmed by the tensile strength. The stress–strain relationship is shown in **Figure 5**, and **Table 3** shows the mechanical properties of the PBAT and PBAT/RMR blends. The blend exhibited brittle characteristics as the RMR content increased, and accordingly, the tensile strength, yield strength, and elongation at break decreased. It is assumed that the shear strength of the 6/4 blend was reduced by changing the fracture mode from adhesive failure to cohesive failure as the hot-melt blends became brittle. However, Young's modulus decreased 8/2 blend and then increased from 7/3 to 6/4 blends. It is because Young's modulus is a factor that can ensure the stiffness of the solid material in blends with a slightly

 $\ensuremath{\textbf{Table 3.}}$  Mechanical properties of tensile test for PBAT and PBAT/RMR blends.

Content	Yield Strength [MPa]	Tensile Strength [MPa]	Young's Modulus [MPa]	Elongation at break [%]
10/0	5.4	12.6	74.7	813.7
9/1	4.1	5.3	45.2	368.4
8/2	3.4	3.7	36.2	320.3
7/3	3.6	3.6	50.9	126.9
6/4	3.6	3.6	77.8	67.8



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Figure 6. a) Molecular weight decreases over time of PBAT and 7/3 blends weight-average molecular weight of from GPC, b) illustration of oriented structure of PBAT and PBAT/RMR blends, and c) crystallinity images of PBAT and PBAT/RMR blends obtained using POM.

increased modulus of 30 wt.% or more (Table 3). The stiffness of the PBAT/RMR blends were relatively decreased, which is assumed to increase the adhesive property owing to molecular chain mobility. However, the adhesive property decreased when the modulus increased above a certain level. Figure 5c illustrates the predicted deformation structure of PBAT and PBAT/RMR. The fracture behavior of PBAT follows a series of mechanisms. First, initial elongation happens mostly in the amorphous regions. Then, the lamellar crystallites start to tilt toward the tensile axis. After that, the crystalline block segments separate and both crystallites and amorphous regions stretch. Finally, this leads to fracture. On the other hand, the inclusion of RMR leads to intermolecular interactions with the PBAT chains. This interaction effectively reduces the attractive forces among PBAT molecules, thereby preventing the formation of lamellar structures. As a result, PBAT/RMR blends display compromised orientation and alignment of molecular chains, making them more brittle under deformation when compared to PBAT. Also, the addition of rosin with a low molecular weight causes a decrease in the overall average molecular weight, thereby weakening the physical properties of the blend and reducing the adhesion due to the influence of the molecular weight. As rosin with a relatively low molecular weight is added, the molecular weight at the adhesive interface is inversely proportional to the chain movement because of its low molecular weight. Therefore, it can be interpreted that this is because the number of molecules that try to adhere to the interface per unit contact area during the same contact period is large.

#### 2.4. Degradation Potential of PBAT Based HMA

The decomposition characteristics of biodegradable polymers are affected by their molecular weight and crystallinity. Polymers with lower molecular weight contain more terminal groups and, therefore, are more easily decomposed by water or enzymes. Further, during degradation, the amorphous region of polymers with low crystallinity undergoes hydrolysis faster than the crystalline region due to their higher rate of water uptake (Figure 6a). The degradation behavior of biodegradable polymers takes place in two stages. First, water diffuses into amorphous regions of the polymer matrix, separating ester bonds. After that, the crystalline segment of the polymer becomes vulnerable to hydrolysis and degradation. Therefore, an increase in the amorphous region affects the biodegradation properties.<sup>[65–70]</sup> The morphological observation of the PBAT/RMR blends mixed by ratio through POM is shown in Figure 6c. As the RMR content increased in the blend, it was observed that the crystal growth of PBAT was disrupted. This led to a decrease in crystallinity and an increase in the amorphous region. Meanwhile, it seems that the presence of amorphous rosin impacts the overall crystallinity of PBAT. In a blend of crystalline and amorphous polymers, the melting point of the crystalline polymer is generally reduced when the two polymers are miscible, and the interaction between the two can be quantitatively assessed based on this decrease in melting point.<sup>[71]</sup>

As the rosin content increases, the regularity of the main chain conformation decreases, resulting in a decrease in the crystalline domain (Figure 6b). This decrease leads to relatively ADVANCED SCIENCE NEWS \_\_\_\_\_\_ www.advancedsciencenews.com

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Scheme 1. a) Schematic diagram of the preparation process of the PBAT/RMR HMA. b) the molecular structure of PBAT and RMR and the possible hydrogen bonds between the PBAT and RMR blend.

more amorphous regions, which improves the flexibility of the chains and enhances the adhesion properties. This relationship between amorphous regions and adhesion properties is shown in Figure 4c,d. In general, the adhesion of the main-chain interface is closely related to the morphology of the contact polymer. An amorphous main chain with a relatively large main chain flexibility easily adheres to the interface compared to that with a crystalline main chain. Therefore, when there are many amorphous regions, the adhesiveness is greater, and it is considered to be significantly affected by the content of the amorphous resin. As a result, PBAT/RMR blends, whose amorphous properties are improved by adding RMR, are considered to have the potential for degradation and an increase in adhesion properties.

## 3. Conclusion

The effect of rosin on PBAT was studied to determine the applicability of the designed HMA and the applicability was confirmed. As a result of the thermal properties, by blending two types of compatible polymers, the two systems formed one phase. As the RMR content increased, the  $T_g$  and  $T_m$  shifted to a single inflection point and peak. Further, it was confirmed that the blend exhibited amorphous characteristics due to the mutual dilution effect of rosin. With respect to the rheological properties, complex viscosity tended to decrease, which can be interpreted as an increase in the adhesion strength owing to improved wettability. Furthermore, through the contact angle results, the wettability of the PBAT/RMR blends was improved that influenced by the relatively hydrophilic properties of rosin. The shear strength of

all the blends to which RMR was added was higher than that of EVA, and it was confirmed that the highest adhesion performance was observed in 7/3 blend. Meanwhile, an increase in rosin content resulted in a stiffening effect on the blends. Accordingly, as the blends became brittle, the failure mode of the lap shear test changed from adhesive failure to cohesive failure, and the adhesive strength decreased. This is because 6/4 reduces adhesive properties. This is considered a cohesive failure as the molecular chain becomes rigid due to the stiffness effect that mentioned in tensile strength properties. By evaluating the properties of the blends themselves through the measurement of the tensile properties, it was possible to support the results of the decrease in adhesive properties. Besides, considering that the amorphousness of polymer compounds improves as the rosin content increases, the decomposition characteristics are expected to increase. Because penetration of the degradation medium is easy because of its low density. Therefore, this study shows that PBAT/RMR blends for eco-friendly HMA, could be replaceable for petroleum-based HMA, showing the industrial applicability.

# 4. Experimental Section

*Materials*: Poly(butylene adipate-co-terephthalate) (PBAT, Solpol 1000NB, Density = 1.26 g mL<sup>-1</sup>) was purchased from Solchemical Co., Ltd, Korea. The polymer was then dried at 60 °C for 12 h and stored in a dry environment. Rosin maleic resin (RMR, DX-250) was purchased from Laton Korea Co. Ltd., Korea.

Preparation of Poly(Butylene adipate-co-terephthalate) and Rosin Maleic Resin Blends: The PBAT was subjected to a drying procedure at 60  $^{\circ}$ C for 12 h before melting. PBAT/Rosin Maleic Resin blends (Scheme 1) were

prepared using a twin-screw extruder (L/D = 40, barrel diameter = 19 mm, BA-19, BAUTEK Co., Ltd., Korea). Various PBAT/RM contents were prepared via a melt-blending technique. Heating zone of the twin-screw extruder was divided into eight barrels. Each baller temperature was set to 140, 160, 160, 160, 160, 140, 100, and 80 °C, form the feed zone to the die zone, with a fixed rotational speed of 100pm. The pellets were pelletized using a pelletizer (BA-20, BAUTEK Co., Ltd, Korea). Five different blends were prepared with different PBAT/RMR weight ratios 0, 10, 20, 30, 40 wt.% and named 10/0, 9/1, 8/2, 7/3, and 6/4.

*Characterization—Thermal properties:* DSC (Q200+RCS90, TA Instrument, Inc., USA) was used to determine the crystallization, glass transition, melting temperatures, and crystallinity. The testing condition was from 30 to 200 °C, and the heat rate of 10 °C min<sup>-1</sup> in a nitrogen atmosphere. The glass transition temperature (T<sub>g</sub>) was calculated using the Fox equation to analyze the compatibility. Where T<sub>g</sub> is PBAT/RM blends, T<sub>g,1</sub>, T<sub>g,2</sub>, and  $\omega_1$ ,  $\omega_2$  are weight fractions of T<sub>g</sub> for the components 1 and 2.

Fox Equation 
$$\left(\frac{1}{T_g}\right) = \frac{\omega_1}{T_{g,1}} + \frac{\omega_2}{T_{g,2}}$$
 (1)

*Rheological properties*: To determine wettability for the complex viscosity and storage modulus, were measured on a rheometer (MCR 302, Anton Paar Ltd, Austria) was used. The diameter of the disposable parallel plate was 25 mm, the plate gap was set to 100  $\mu$ m, and the shear strain was 5%. In oscillatory mode in the linear viscoelastic domain at a frequency of 10 rad s<sup>-1</sup> and 160 °C.

Contact angle: The Contact angles (CA) of the PBAT and PBAT/RM blends were measured using an electrical testing instrument (SEO 300A contact angle measuring device, Surface & Electro-Optics Co., Korea) to determine surface wettability. Deionized water and diiodomethane were used as the test liquids, and  $\approx 6 \,\mu$ m drops were slowly placed on the dried film. Images were recorded immediately after the droplet was disposed of on the surface of each sample.

*FT-IR*: The Fourier Transform Infrared spectra analysis of blends spectra was recorded on Nicolet iS20 FTIR, Thermo Fisher Scientific, Inc., USA). All samples were measured in the range of 4000–500 cm<sup>-1</sup> with resolution of 2cm<sup>-1</sup> and 16 scans.

*Mechanical properties*: The lap shear and tensile strengths of the PBAT/RMR composites were determined using seven samples in dumbbell shapes (ASTM D-638, Type V) of each composition on a Universal Testing Machine (UTM Z010, Zwick, Inc., Germany) at a constant cross-speed of 25 mm min<sup>-1</sup>. The average values were calculated by taking the mean of five runs.

Biodegradability: The crystallization behavior of the samples was observed using a polarizing microscope (POM; Eclipse LV100ND, Nikon Instrument, Inc., Japan). The sample was placed between the slide and cover glass, completely melted at 160 °C for 15 min, and then cooled to room temperature (23 °C) to measure the change in the brightness of light due to crystal growth. The molecular weight of hydrolyzed PBAT and PBAT/RMR blend was characterized by The molecular weight of the hydrolyzed PBAT and PBAT/RMR blend was characterized by Gel permeation chromatography (GPC, NEXERA, SHIMADZU, Inc, Japan) equipped with an RID-20A detector. All the samples were diluted with tetrahydrofuran to 0.2 wt.% concentration. The molecular weight was calculated using a polystyrene standard. To characterize the GPC, the polymer solution was dissolved in tetrahydrofuran at a concentration of 0.2 wt.% for 24 h. The dissolved solution was then filtered using a stainless steel mesh with a hole size of  $\approx$ 74  $\mu$ m, and the filtered polymer solution was characterized.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

# **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## **Keywords**

adhesion properties, eco-friendly hot melt adhesive, hot-melt adhesive (HMA), Poly(butylene adipate-co-terephthalate)

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