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# New Composition of Maleic-Anhydride-Grafted Poly(Lactic Acid)/Rice Husk with Methylenediphenyl Diisocyanate

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Maleic-anhydride-grafted poly(lactic acid) (PLA-g-MAH) was prepared and blended with rice husk (RH). Methylenediphenyl diisocyanate (MDI) was used as the coupling agent for combining RH with PLA-g-MAH, which improved the poor interfacial adhesion between PLA and RH. Various PLA-g-MAH/RH blends, with and without MDI, were prepared by melt processing using a brabender. The effects that inclusion and distribution of MDI had on the mechanical properties and thermal behaviors of the composites were examined. The results showed that the $PLA_XRH_YMDI$ specimens had the optimum tensile properties compared with the $PLA_XRH_Y$, PLA-g-$MAH_XRH_Y$, and PLA-g-$MAH_XRH_YMDI$ specimens. The new method of combining MDI and MAH through grafting was expected to be an excellent strategy for mitigating the low functionality of commercial PLA. Possible reasons accounting for the interesting results on tensile strength and thermal properties of the specimens are proposed.

*Keywords*: poly(lactic acid), rice husk, maleic-anhydride, methylenediphenyl diisocyanate.

## 1. INTRODUCTION

Poly(lactic acid) (PLA), produced annually from renewable biofeedstocks such as corn, is one of the most important bio-based biodegradable materials that are now applied to numerous commercial applications. Despite promising properties of PLA, its high production costs, poor impact strength, and severe brittleness have restricted its applicability and production capability. Moreover, the price competitiveness of PLA in the biodegradable plastic market is an essential attribute that cannot be ignored. The most effective approach to reduce the capital cost of PLA is to use fillers. Cost-effective reinforcements are organic renewable resources [1], flax [2–4], sisal [5], lyocell [6], short abaca [7], jute [8], bamboo [9], paper pulp [10, 11], pineapple [12], cordenka [13], and microcrystalline cellulose [14]. Rice husk (RH) is attractive because of its low cost, renewability, biodegradability, low density, and non-abrasiveness. A number of researches on synthetic polymers and rice husk composites [15–19] have been reported. Their incorporation into hydrophobic thermoplastic polymers typically results in poor dispersion, high viscosity, and low compatibility. The poor interfacial adhesion between the filler and the matrix generally leads to composites with worse mechanical properties. Surface and bulk modifications of the filler and/or matrix are necessary to increase the interfacial compatibility between the hydrophilic lignocellulosic filler and the hydrophobic PLA matrix. Some studies used methylenediphenyl diisocyanate (MDI) as a compatibilizer to improve the interfacial compatibility of PLA and starch [20, 21], or tapioca[22].These biopolymers are successfully prepared with starch blends using methylenediphenyl diisocyanate (MDI) as a coupling agent, which is effective because of the formation of urethane linkages between the –NCO groups of MDI and the –COOH groups of PLA and between the –NCO groups and the –OH groups of starch. In this study, we followed the idea of using MDI as a coupling agent to improve the interfacial compatibility between PLA and RH. The structure of PLA shows that it has a –COOH functional group at the end of its molecular chain. Certain studies have reported on how to make the functional groups of PLA compatible with starch; one way is to graft maleic anhydride (MAH) and acrylic acid (AA) onto PLA [23, 24]. In this study, we adopted two

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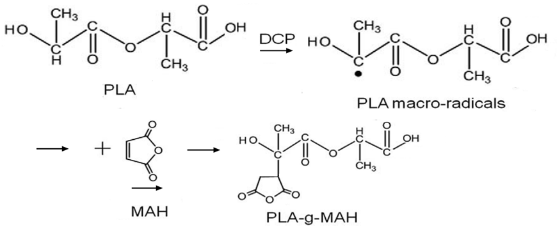
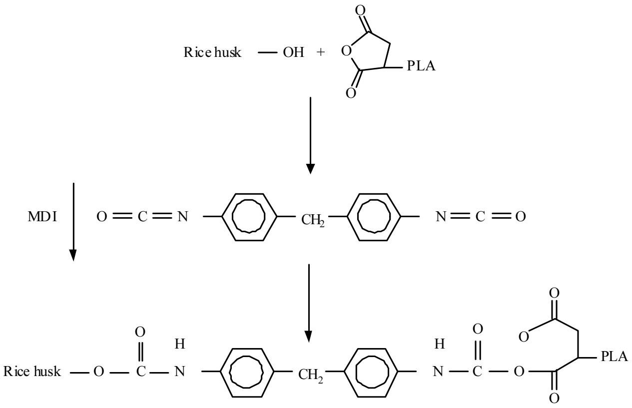
approaches to improve the bonding ability between PLA and RH: first was either grafting or adding a coupling agent, and second was using both methods. We also reported the comparison between the PLA-g-MAH/RH with MDI and that without MDI. As shown in Scheme 1, it is possible mechanism for grafting MAH onto PLA. Scheme 2, it is possible to effectively enhance the compatibilization between RH and PLA-g-MAH.



**Scheme 1.** Possible mechanism for grafting MAH onto PLA



**Scheme 2.** Possible mechanism for reaction of MDI with rice husk and PLA-g-MAH

## 2. EXPERIMENTAL

### 2.1. Materials and preparation

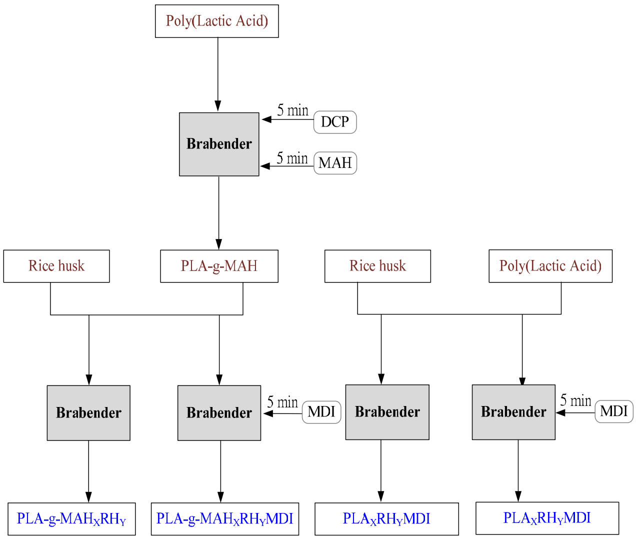
Before preparing PLA$_X$RH$_Y$, the rice husk (RH) powder was dried at 80 ºC for 2 h and then further dried at 120 ºC for 4 h. The RH was collected from a local farm factory. In preparing NaOH solutions at different concentrations of RH, NaOH solution was mixed with the RH that was not dried at a ratio of 1 : 5 (RH : NaOH). The mixtures were then stirred for 1 h and neutralized with distilled water. The neutralized solutions were then filtered. The filtrates were dried by blast drying at 105 ºC for 2 h and then further dried at 120 ºC for 4 h. The dried RH particles were separated using a sieve, which sorted particle sizes below 0.25 mm. After drying, the selected particles were then blended with PLA. The PLA resin used in this study, with a trademark name Nature green 4032D, was obtained from Cargill-Dow. The blends were prepared in a brabender with a blade speed of 80 rpm at 180 ºC. Initially, the PLA was melted inside the blender; after which, DCP and MAH (purchased from Sigma-Aldrich, Taiwan) were added and reacted with the PLA for optimal duration (1 phr DCP, 2.5 phr MAH). Then, the blending reaction with RH lasted for a few minutes, with and without 1 phr MDI (MDI, a dark brown viscous liquid, was purchased from ICI Polyurethanes Group, West Deptford, NJ). The prepared PLA/RH specimens were hot-pressed at 190 ºC and 10 MPa for 2 min and then cooled in air at approximately 25 ºC. The compositions and procedures of the all specimens prepared in this study are summarized in Table 1 and Scheme 3, respetively. Before hot-pressing, the specimens were dried in a vacuum oven at 80 ºC for 12 h.

### 2.2. Fourier transform infra-red spectroscopy (FTIR)

FTIR measurements were performed on a PerkinElmer spectrometer, model Spectrum One. Spectra of the samples were obtained by averaging 15 scans with a wave number range of 4000 cm$^{-1}$ to 650 cm$^{-1}$ and a resolution of 2 cm$^{-1}$.

**Table 1.** Compositions of PLA, PLA$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$MDI, and PLA$_X$RH$_Y$MDI specimens

| Samples | PLA (%) | RH (%) | MAH (phr) | DCP (phr) | MDI (%) |
|---|---|---|---|---|---|
| PLA | 100 | – | – | – | – |
| PLA$_{90}$RH$_{10}$ | 90 | 10 | – | – | – |
| PLA$_{80}$RH$_{20}$ | 80 | 20 | – | – | – |
| PLA$_{70}$RH$_{30}$ | 70 | 30 | – | – | – |
| PLA$_{60}$RH$_{40}$ | 60 | 40 | – | – | – |
| PLA$_{50}$RH$_{50}$ | 50 | 50 | – | – | – |
| PLA-g-MAH$_{90}$RH$_{10}$ | 90 | 10 | 2.5 | 1 | – |
| PLA-g-MAH$_{80}$RH$_{20}$ | 80 | 20 | 2.5 | 1 | – |
| PLA-g-MAH$_{70}$RH$_{30}$ | 70 | 30 | 2.5 | 1 | – |
| PLA-g-MAH$_{60}$RH$_{40}$ | 60 | 40 | 2.5 | 1 | – |
| PLA-g-MAH$_{50}$RH$_{50}$ | 50 | 50 | 2.5 | 1 | – |
| PLA-g-MAH$_{90}$RH$_{10}$MDI | 90 | 10 | 2.5 | 1 | 1 |
| PLA-g-MAH$_{80}$RH$_{20}$MDI | 80 | 20 | 2.5 | 1 | 1 |
| PLA-g-MAH$_{70}$RH$_{30}$MDI | 70 | 30 | 2.5 | 1 | 1 |
| PLA-g-MAH$_{60}$RH$_{40}$MDI | 60 | 40 | 2.5 | 1 | 1 |
| PLA-g-MAH$_{50}$RH$_{50}$MDI | 50 | 50 | 2.5 | 1 | 1 |
| PLA$_{90}$RH$_{10}$MDI | 90 | 10 | – | – | 1 |
| PLA$_{80}$RH$_{20}$MDI | 80 | 20 | – | – | 1 |
| PLA$_{70}$RH$_{30}$MDI | 70 | 30 | – | – | 1 |
| PLA$_{60}$RH$_{40}$MDI | 60 | 40 | – | – | 1 |
| PLA$_{50}$RH$_{50}$MDI | 50 | 50 | – | – | 1 |



**Scheme 3.** Preparation of PLA$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$MDI, and PLA$_X$RH$_Y$MDI specimens

### 2.3. Mechanical properties

The tensile properties of the hot-pressed PLA, PLA/RH, PLA-g-MAH/RH, and PLA-g-MAH/MDI/RH specimens at 25 ºC were determined using a Shimadzu tensile testing machine (model AG-10KNA) with a crosshead speed of 50 mm/min. A 35-mm gauge length was used for each tensile experiment. The dog-bone-shaped specimens were prepared according to the ASTM D638 Type IV standard. The values of tensile strength and elongation at break were obtained based on the average tensile results of at least five tensile specimens.

## 2.4. Differential scanning calorimetry (DSC)

The thermal properties of the PLA composites resins were determined using a TA Q100 differential scanning calorimetry (DSC) instrument. All DSC scans were performed at a heating rate of 10 ºC/min and under flowing nitrogen with a flow rate of 50 mL/min. The instrument was calibrated using pure indium. Samples weighing approximately 15 mg and 0.5 mg were placed in standard aluminum sample pans for $T_g$ and $T_m$ determination of each specimen, respectively.

## 2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed by using a PerkinElmer TGA, model Pyris 1. Samples (8 – 10 mg) under nitrogen were heated at a rate of 10 ºC/min from room temperature to 600 ºC.

## 3. RESULTS AND DISCUSSION

## 3.1. Fourier Transform Infrared Spectrometer (FTIR)

Fig. 1 shows the FTIR spectra of RH, PLA, $PLA_XRH_Y$, PLA-g-$MAH_XRH_Y$, PLA-g-$MAH_XRH_Y$MDI, and $PLA_XRH_Y$MDI. To qualitatively indicate the reaction of MAH with PLA, we obtained the FTIR spectra of PLA, MAH, PLA-g-MAH, and PLA-g-MAH, as shown in Fig. 1. The peaks in the range of 1260 $cm^{-1}$ and 1020 $cm^{-1}$ are attributed to –C–O– stretching and –C–C– stretching, respectively. Sclavons et al. [25] indicated that the two typical C=O stretching modes of anhydride at approximately 1756 $cm^{-1}$ suggested the presence of MA. In this study, the peak at 1756 $cm^{-1}$ corresponds to the –C=O stretching of MAH. The peak at 1744 $cm^{-1}$ is the assignment of –C=O carbonyl stretching. The peak at 1451 $cm^{-1}$ is assigned as –C–H–deformation, whereas 1380 $cm^{-1}$ and 1360 $cm^{-1}$ correspond to the C–O–H band. The peaks detected at 1632, 1585, and 1563 $cm^{-1}$ are associated with –C=C stretching. The 1260 $cm^{-1}$ peak is attributed to the –C–O stretching of the anhydride group from MAH. The band at 1756 $cm^{-1}$ corresponds to the succinate anhydride group, whereas 1850 $cm^{-1}$ can be assigned to the symmetric (strong) and asymmetric (weak) stretching vibrations of C=O [1]. The FTIR spectra of PLA-g-MAH indicate that the increase in the –C=O carbonyl stretching for PLA-g-MAH is due to the rising DCP content. A few new peaks appear in the range of 1638 – 1608, 1585, and 1458 $cm^{-1}$ for the PLA-g-MAH in this study (see Fig. 1, d). The absorption bands at 1638 $cm^{-1}$ – 1608 $cm^{-1}$ correspond to the C=O stretching from the anhydride groups of MAH. The peaks at 1585 $cm^{-1}$ and 1458 $cm^{-1}$ are assigned to C=C stretching and $–CH_2–$ deformation, respectively. MAH was successfully grafted onto PLA. The FTIR spectra of $PLA_XRH_Y$MDI (Fig. 1, f) indicate that the 2290 $cm^{-1}$ peak is attributed to the –N=C=O stretching of the MDI. The peak at 3310 $cm^{-1}$ is the –NH bending due to the reaction between the –OH group of RH and the –N=C=O group of MDI, resulting in the formation of the urethane group. Fig. 1, e, shows that the peaks of PLA-g-$MAH_XRH_Y$MDI at 3200 $cm^{-1}$ to 3600 $cm^{-1}$ are similar to PLA-g-$MAH_XRH_Y$; the peak at 2290 $cm^{-1}$ does not appear. This interesting result might be because most of the cyanic acid groups (–N=C=O) are reacted with the $COO^-$ group of PLA-g-$MAH_XRH_Y$; thus, there is not enough –N=C=O group to react with the –OH group of RH.

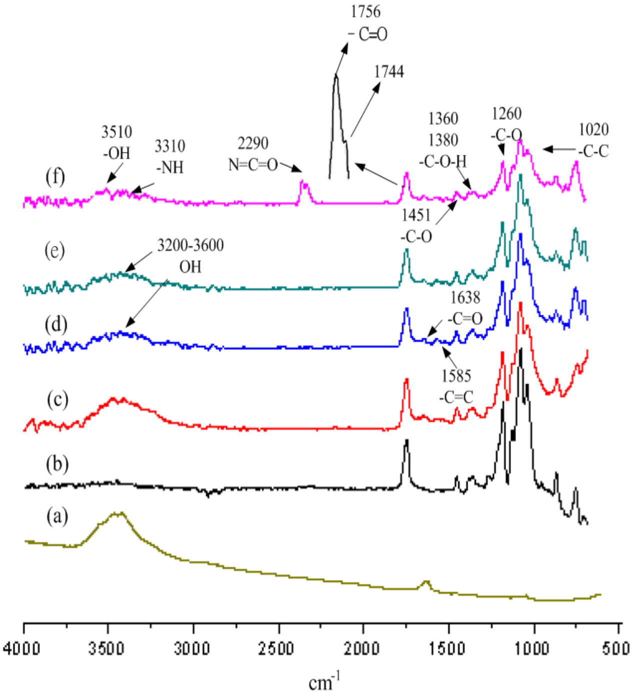


**Fig. 1.** FTIR of RH (a), PLA (b), $PLA_{70}RH_{30}$ (c), PLA-g-$MAH_{70}RH_{30}$ (d), PLA-g-$MAH_{70}RH_{30}$MDI (e), and $PLA_{70}RH_{30}$MDI (f)

## 3.2. Tensile Properties

The tensile strength of pure PLA and the specimens with varying RH content (PLA-g-MAH, PLA-g-MAH/MDI, and PLA/MDI) is shown in Fig. 2. The tensile strength ($\sigma_f$) of $PLA_XRH_Y$ specimens decreased from 58.4 MPa to 14.3 MPa as the RH content increased from 0 wt% to 50 wt%. This is consistent with the polar surface of RH, in its unlikelihood of interacting strongly with the less polar PLA host matrix [26]. In contrast, the $\sigma_f$ value of PLA-g-$MAH_XRH_Y$ specimens increased slightly with the RH content and reached a maximal value at 24.6 MPa as their RH content approached 50 wt%. However, the $\sigma_f$ value of PLA-g-MAH/RH/MDI specimens was similar as their RH content increased from 10 wt% to 50 wt%; the value was 32.8 MPa when their content reached 50 wt%. The $\sigma_f$ values of PLA-g-$MAH_XRH_Y$MDI specimens were higher than those of PLA-g-$MAH_XRH_Y$. The $\sigma_f$ value of PLA-g-$MAH_{50}RH_{50}$MDI compared with $PLA_XRH_Y$ was higher, which was about 229 %. This improvement in the $\sigma_f$ value is due to an increase in the PLA/RH interfacial adhesion caused by the formation of urethane linkages between MDI and PLA-g-MAH, as well as those between MDI and RH, because MDI acts as a coupling agent. In addition, the $\sigma_f$

values of PLA$_X$RH$_Y$MDI were significantly higher than the other specimen series; the values were 50.3 MPa to 50.7 MPa when the RH content increased from 10 wt% to 50 wt%. The $\sigma_\mathrm{f}$ values of the various specimen series are listed in descending order: PLA$_X$RH$_Y$MDI > PLA-g-MAH$_X$RH$_Y$MDI > PLA-g-MAH$_X$RH$_Y$ > PLA$_X$RH$_Y$. This indicates that the new method of combining MDI and MAH through grafting is worse than using MDI as a coupling agent only.

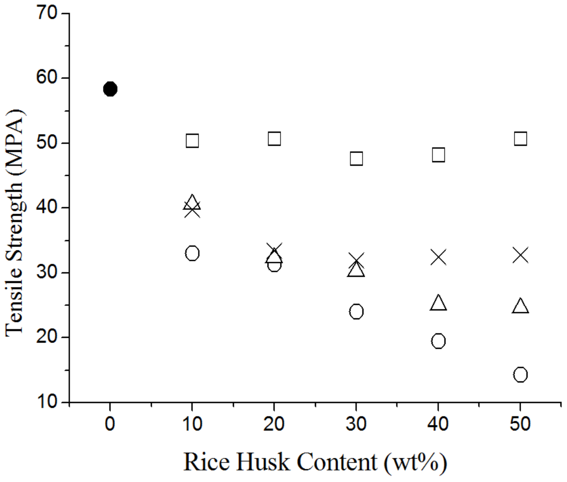
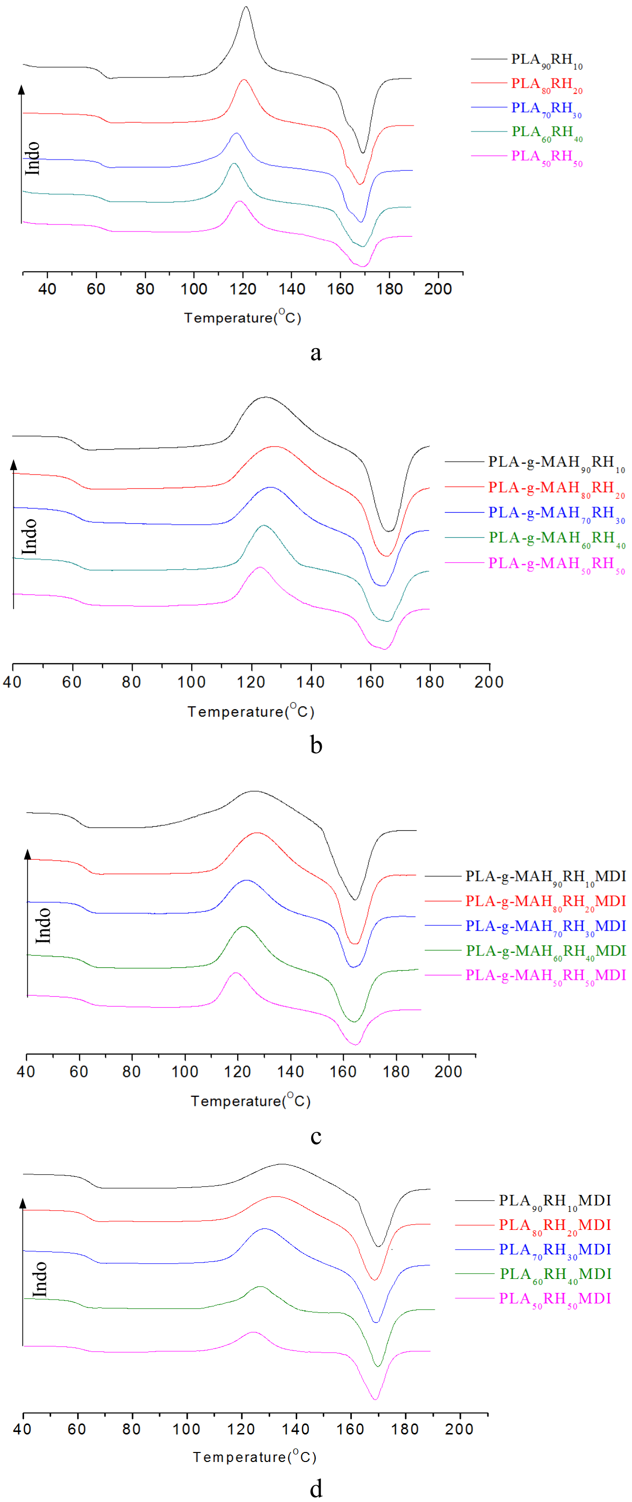


**Fig. 2.** Tensile strength: (●) – PLA, (○) – PLA$_X$ RH$_Y$PLA, (Δ) – PLA-g-MAH$_X$RH$_Y$, (×) – PLA-g-MAH$_{70}$RH$_{30}$MDI, (□) – PLA$_{70}$RH$_{30}$MDI

### 3.3. DSC Analysis

The DSC analysis of the PLA$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$MDI, and PLA$_X$RH$_Y$MDI specimens is shown in Fig. 3. The thermograms were obtained from the second heating scan to avoid the effects of the heat history. Fig. 3, a, shows the melting behaviors of PLA$_X$RH$_Y$; there were second melting temperatures ($T_\mathrm{m}$) for PLA$_X$RH$_Y$ specimens, due to the incompatibility of PLA and RH with each other. The second melting temperatures were slightly decreased after grafting PLA with MAH (see Fig. 3, b). Fig. 3, c, demonstrates that the second $T_\mathrm{m}$ of PLA-g-MAH$_X$RH$_Y$ did not appear after MDI was added. The $T_\mathrm{m}$ peaks of PLA-g-MAH$_X$RH$_Y$MDI were narrower than PLA$_X$RH$_Y$ and PLA-g-MAH$_X$RH$_Y$; it is because MDI, being a successful coupling agent between the COO$^-$ group of PLA and the NCO group of MDI, makes it more compatible. In addition, Fig. 3, d, indicates that the $T_\mathrm{m}$ of PLA$_X$RH$_Y$MDI had only single peaks as well; the peaks were sharper and narrower than the peaks of PLA-g-MAH$_X$RH$_Y$MDI, demonstrating that the combination of grafting MAH onto PLA and adding MDI is not a better way of blending PLA and RH.



a

b

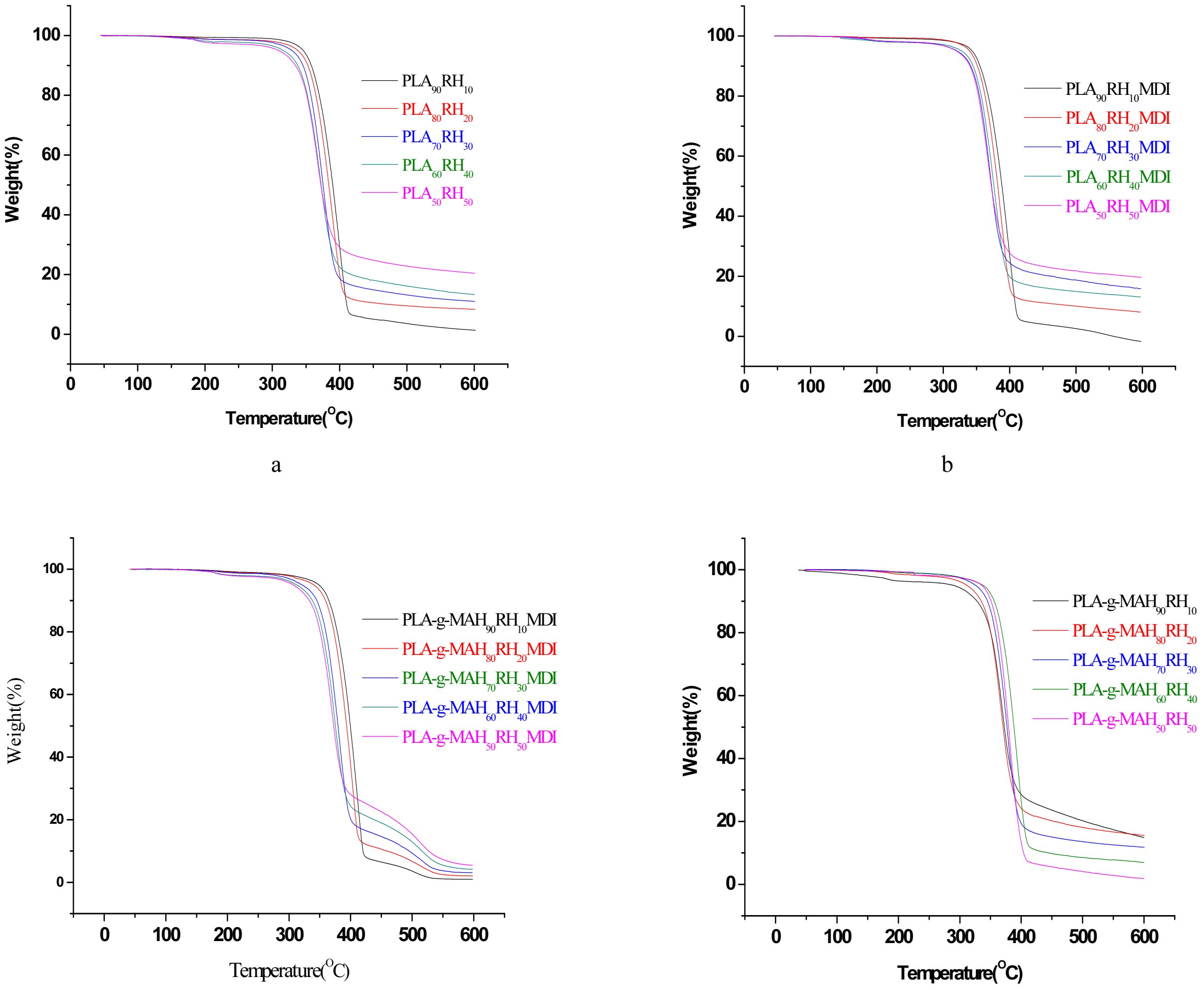
c

d

**Fig. 3.** DSC of PLA$_X$RH$_Y$PLA (a), PLA-g-MAH$_X$RH$_Y$ (b), PLA-g-MAH$_X$RH$_Y$DI (c), and PLA$_X$RH$_Y$MDI (d)

### 3.4. TGA analysis

The thermal stability of PLA$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$, and PLA-g-MAH$_X$RH$_Y$MDI, PLA$_X$RH$_Y$MDI was investigated with thermogravimetric (TGA) analysis. Fig. 4, a, shows the TGA curves for PLA$_X$RH$_Y$, which indicates that the final char residue increased significantly from 3.5 wt% to 22.8 wt% after the RH content was increased from 10 wt% to 50 wt%, but the decomposition temperature decreased from 366.2 to 344.3°C when the RH content was increased from 10 wt% to 50 wt%. The addition of RH decreased the thermal stability of the neat PLA, since some portion of the polymer (PLA) was replaced with less thermally stable material (natural fibers). This is a common trend and generally approves that the addition of natural fibers reduces the thermal stability of a polymer matrix [27, 28]. TGA results in Fig. 4. b, c and d, show that the trend of the thermal decomposition temperature of PLA-g-MAH$_X$RH$_Y$,PLA-g-MAH$_X$RH$_Y$MDI, and PLA$_X$RH$_Y$MDI is similar to PLA$_X$RH$_Y$. The decomposition temperature of



a b

c d

**Fig. 4** TGA of (a) PLA$_X$RH$_Y$PLA, (b) PLA-g-MAH$_X$RH$_Y$, (c) PLA-g-MAH$_X$RH$_Y$DI, (d) PLA$_X$RH$_Y$MDI.

## 4. CONCLUSIONS

Four series of specimens, PLA$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$, PLA-g-MAH$_X$RH$_Y$MDI, and PLA$_X$RH$_Y$MDI, were utilized to prepare PLA composites; their mechanical and thermal properties were studied and compared. It was found that $\sigma_f$ values of PLA$_X$RH$_Y$ drastically increased when grafting MAH onto PLA was combined with MDI as a coupling agent. The DSC analysis of PLA$_X$RH$_Y$ indicated the appearance of the second melting temperatures ($T_m$) for the PLA$_X$RH$_Y$ specimens, due to the incompatibility between PLA and RH. The compatibilities were improved after MAH was grafted onto PLA and/or using MDI as a coupling agent. The DSC analysis of PLA$_X$RH$_Y$MDI indicated that the $T_m$ peaks were only single, and they were sharper and narrower than the peaks of PLA-g-MAH$_X$RH$_Y$MDI. For the $T_m$ peaks of PLA$_X$RH$_Y$MDI with high compatibility exhibit the narrower distributions, it is due to the MDI that reacted to PLA and RH to enhance incompatible parts of PLA$_X$RH$_Y$ whose peaks had been supposed the second $T_m$. For PLA-g-MAH$_X$RH$_Y$MDI, might be attributed to parts of over coupling between the COO$^-$ group of MAH and the NCO group of MDI. Thus, PLA-g-MAH$_X$RH$_Y$MDI exhibit broader distributions. It demonstrated that the compatibility of the PLA$_X$RH$_Y$MDI series was the best in this study. FTIR analysis indicated that most of the cyanic acid groups (–N=C=O) reacted with the COO$^-$ group of the PLA-g-MAH$_X$RH$_Y$; thus, there was not enough –N=C=O group to react with the –OH group of RH. The PLA might overdose coupling between the grafted MAH and MDI. This result was consistent with the appearance of the new decomposition stage (400 °C to 550 °C) for PLA-g-MAH$_X$RH$_Y$MDI based on the TGA analysis. According to the above reasons, the combination of grafting MAH onto PLA and using MDI as a coupling agent was not an appropriate method for PLA and RH.

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