

Characterization of hydrolytic degradation of polylactic acid/rice hulls composites in water at different temperatures

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Abstract. Hydrolytic degradations of polylactic acid/rice hulls (PLA/RH) composites with various rice hulls contents due to water absorptions at 23, 51 and 69°C were investigated by studying the thermal properties, chemical composition, molecular weight, and morphology of the degraded products. The results have attested that the stability of PLA/RH composites in water depends slightly on rice hulls contents but it is significantly influenced by water temperature. Water absorption in 30 days at 23°C was between 0.87 and 9.25% depending on rice hull contents. However, at thermophilic temperatures, the water absorption and degradation of these products were increased significantly. Saturations were achieved in less than 25 and 9 days at 51°C and 69°C, respectively, while hydrolytic degradation was demonstrated by an increase in fragility and development of crystallinity. At 69°C, there were significant reductions of the decomposition and glass transition temperatures of the polymer by 13°C. These changes were associated with the reduction of the molecular weight of PLA from 153.1 kDa to ~10.7 kDa due to hydrolysis of its ester group.

Keywords: biodegradable polymers, polylactic acid, rice hulls, hydrolytic degradation, molecular weight

1. Introduction

There has been a growing interest in the development of environmentally benign composites based on biodegradable poly(lactic acid) (PLA) polymer and various lignocellulosic materials such as kenaf [1, 2], flax [3], hemp [4], bamboo [5, 6], wood fibers [7], and reed fibers [8]. Addition of lignocellulosic materials in PLA is intended to improve the properties of this polymer without compromising its biodegradability. Although there has been very little work in the development of biodegradable polymer composites using rice hulls [1], several studies have demonstrated the potential of rice hulls in polymer composites [9–13]. Rice hulls are siliceous lignocellulosic residues, which have moderate water resistance and stability against degradation. It may

be interesting therefore to find out how these properties can affect the biodegradability of PLA.

PLA is a biodegradable polymer, which is naturally hydrophilic due to its polar oxygen linkages. It contains a methyl side group, which confers hydrophobic properties to this polymer [14]. The natural hydrophilic characteristic of PLA is responsible for its moderate decomposition in accordance with the surrounding moisture and temperature. The first stage of PLA degradation is usually the reduction of its molecular weight by hydrolysis to <10 kDa before it becomes biodegradable. The hydrolysis of PLA occurs by random cleavage of the –C–O– ester bond by water molecules. The hydrolysis products, which may contain fragments of lactic acid, oligomers and other water soluble products, can then be con-

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sumed by microorganisms to produce carbon dioxide (CO₂), water (H₂O) and solid biomass [15]. This reaction can be increased under acidic or basic conditions or in the presence of high moisture and high temperature [16, 17]. Previous studies have shown that PLA is moderately stable in water at mesophilic temperatures (15–40°C). It can absorb between 0.7 and 1% of water in 30 days [18] or slightly higher at longer immersion periods [2] at these temperatures. The absorption of water by PLA biocomposites at these temperatures can lead to moderate change in their properties depending on filler contents [2, 18]. Since hydrolysis of PLA is influenced by ambient moisture and temperature, it is possible to accelerate the diffusion of water and hence increase the hydrolysis or degradation of this polymer by subjecting it to thermophilic temperatures above 50°C. In this report, the degradation of PLA/RH composites due to water absorption at 23, 51 and 69°C was investigated. The tests were carried out by immersing the PLA products in water until they were completely saturated. Their degradation was studied by thermal analysis, infrared spectroscopy, molecular weight analysis, and surface morphology analysis.

2. Materials and methods

2.1. Materials and preparations

Rice hulls were obtained from rice mills in Tanzania. A commercial grade PLA (Ingeo 3051D) in pellets form with a melt flow index of 1–2.5 g/min, from RESINEX Nordic AB Sweden, was used as a resin. The resin had the following specifications: specific gravity 1.24; melting temperature between 145 and 155°C, crystallization temperature from 95 to 120°C and the glass transition temperature ranging from 55 to 58°C. Dicumyl peroxide (DCP)-98% (Aldrich) and maleic anhydride (MA) briquettes M188-99% (Aldrich), purchased from Sigma Aldrich Sweden AB, were used as free radical initiator and coupling agent, respectively.

The PLA polymer and MA were prepared separately by grinding through a 1 mm sieve. The rice hulls (RH) were also ground through a 1-mm sieve and were dried overnight in an oven at 102°C to remove residual moisture. The ground rice hulls were designated as untreated rice hulls (URH).

2.2. Preparation of the composites

The composites were prepared by mixing different ratios of ground PLA resin and dry rice hulls. The amount of MA in the composites was controlled by the proportion of RH (i.e. 7% RH) while DCP was fixed at 7% MA. The mixture was tumbled in a mechanical mixer that rotates in three axes for about 30 minutes. This was followed by vacuum drying the mixture at 80°C for about 6 hours and then pressing under vacuum in a 400 kN compression moulding machine (Fontune Presses) at 190°C and 10 MPa for 5 minutes to produce 140 mm × 52 mm × 2 mm PLA composites with various contents of rice hulls. The PLA without rice hulls was designated as PLA-100 and those which contained the rice hulls were designated as PLA/URH 80/20, PLA/URH 70/30 and PLA/URH 60/40 where the digits refer to the proportion of PLA and RH in the composites, respectively.

2.3. Water absorption test

Water absorption tests were carried out in accordance with ASTM D570-98 guideline by submerging five rectangular test specimens with 20 × 50 × 2 mm³ dimensions into water at 23±1°C, 51±0.5°C and 69±1°C until they were completely saturated. All test specimens were dried in a conventional oven at 51±0.5°C for 24 hours prior to immersion in water. The test specimens were periodically removed from water and dried thoroughly with tissue papers before recording their weight gains. After saturation, all the test specimens were redried to constant weights at 51±0.5°C for 24 hours at the end of the test.

Absorption of water into the polymer composite is controlled by diffusion. If the diffusion follows Fickian behavior, an increase in weight can be described in terms of the diffusion coefficient, D , and the maximum moisture content, M_m as shown by Equation (1) [5, 18].

$$\frac{M_t}{M_m} = \frac{4}{h} \left(\frac{D}{\pi} \right)^{1/2} \cdot t^{1/2} \quad (1)$$

where M_t is the degree of water-sorption at time t ; M_m is the water-sorption amount at equilibrium sorption time; h is the thickness of the specimen; and t is the water-sorption time.

The diffusion coefficient, D , may be given by Equation (2) from the slope (k) of the initial linear portion of the absorption curve M_t against $t^{1/2}$.

$$D = \pi \left(\frac{kh}{4M_m} \right)^2 \quad (2)$$

2.4. Visual inspection of physical changes

Changes in the physical appearance such as color and flexibility of the test specimens were also monitored during the test.

2.5. Infrared spectroscopy analysis

Hydrolytic degradations of PLA and PLA/RH composites with different contents of rice hulls were also studied by infrared spectroscopy using a Fourier Transform Infrared (FTIR)-spectrometer 2000 system (Perkin Elmer). Each sample was run in duplicate and the results presented are the average of two runs. Samples were dried at $51 \pm 0.5^\circ\text{C}$ for 24 hours before the analysis.

2.6. Thermal analysis

The influence of hydrolytic degradation on the thermal transitions and thermal stability of PLA and PLA/RH composites was determined by scanning calorimetry 1 (DSC1) and thermal gravimetric analysis (TGA) TGA/SDTA851 systems (Mettler Toledo AB, Sweden). The DSC1 system was calibrated using the melting temperature and enthalpy of indium as standard. The control samples from the non-immersed PLA and PLA/RH composites were ground through 1 mm test sieve while those from water soaked PLA and the PLA/RH composites were cut or crushed by hand. All test samples were accurately weighed into 100 μl aluminium pans to within 8.50 mg. An empty pan was used as a reference and each test sample was run in duplicate. The test was started by holding the samples at 25°C for 5 minutes and then raising the temperature to 200°C at $10^\circ\text{C}/\text{min}$ under 50 ml/min of N_2 gas. The samples were isothermally heated at 200°C for 3 minutes and subsequently cooled back to 25°C at $-10^\circ\text{C}/\text{min}$ and held at that temperature for 3 minutes before heating again at the same rate to 200°C . All DSC measurements were taken from the second heat cycle in order to eliminate the influence of sample history.

Crystallinity of the PLA polymer was calculated from the DSC results using the melting enthalpy (ΔH_m^*) of a pure crystalline PLA. The ΔH_m^* value used to estimate the crystallinity is either 135 J/g suggested by Mitaya and Masuko [19] or 93.7 J/g calculated by Fischer *et al.* [20]. In this study, Mitaya and Masuko's value was used in conjunction with the Equation (3), which has been used elsewhere [21].

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^*} \cdot 100\% \quad (3)$$

where ΔH_m is the melting enthalpy of PLA in the composite.

Thermal stability measurements of the PLA and PLA/RH composites were carried out between 25°C and 700°C at $10^\circ\text{C}/\text{min}$ under N_2 environment at 50 ml/min using TGA technique. The sample weight was maintained within 12.0 ± 0.5 mg. The samples were initially dried at $51 \pm 0.5^\circ\text{C}$ for 24 hours before the analysis.

2.7. Molecular weight analysis

Molecular weights reduction of PLA due to water absorptions were measured by TripleSEC Size Exclusion Chromatography (SEC) system using THF (1.0 ml/min) as the mobile phase was performed at 35°C using a Viscotek TDA model 301 equipped with two T5000 columns with porous styrene divinylbenzene copolymer (300 mm $L \times 7.8$ mm ID, exclusion limit MW polystyrene: 400 000 kDa) from Malvern (UK), a VE 2500 GPC autosampler, a VE 1121 GPC solvent pump, and a VE 5710 GPC degasser from Viscotek Corp. (the Netherlands). The samples were prepared by dissolving ~ 20 mg of PLA into 10 ml of THF. After filtration, the samples were transferred into 2 ml vials for analysis.

2.8. Morphological analysis

The influence of hydrolytic degradation on the fracture surfaces of PLA and PLA/RH composites was examined by Hitachi Field Emission SEM S-4800 system (Spectral Solutions AB, Sweden). The observations were made on the cross sections of the fracture surfaces of gold sputtered samples and also on the surfaces of these samples, which were in contact with water. All samples were prepared by breaking

with hand except those that were immersed at 23°C, which required freeze-drying in liquid nitrogen prior to breaking.

3. Results and discussion

3.1. Water absorption and physical changes

Figures 1a to 1c show the results of water absorption by PLA and PLA/RH composites at 23, 51 and 69°C, respectively. The diffusion of water into these products was higher during the first periods and decreased gradually until they were saturated suggesting a classical Fickian diffusion phenomenon. A mixed diffusion behavior has been reported previously in other PLA products [5, 18, 2]. However, it is shown that most of the PLA products that were immersed at 69°C (Figure 1c) did not reveal consistent saturations and therefore failed to exhibit Fickian diffusion phenomenon. At 51 and 69°C temper-

atures, the PLA/RH composites did not stabilize long at the saturation points and the time to reach that saturation was also significantly reduced. This was probably due to increased hydrolysis and leaching of the rice hulls and water soluble polymer products from the composites. Visual observations revealed that PLA products, which were immersed at 69°C, lost the transparency and became fragile from the third day. The composites that were immersed at 51 and 69°C became fragile during the testing period. On the contrary, the PLA products that were immersed at 51°C developed hardness while undergoing hydrolysis. This physical anomaly was examined by studying the morphologies of the fracture surfaces of all PLA and PLA/RH composites. PLA products are generally stable against hydrolysis at mesophilic temperatures [15] and absorb little amount of water [2, 18]. However, the results have attested that the hydrolysis and water absorption of these products can be accelerated significantly by simply subjecting them above the softening temperature of PLA.

By using the classical Fickian diffusion phenomenon, it was possible to estimate the diffusion parameters of some of the composites, which exhibited this behavior. The results shown in Table 1 generally corroborate the proposition that the rate of water diffusion into the composites increases at higher immersion temperatures with the exception of PLA and PLA/RH composites with 40% rice hulls content (PLA/URH 60/40) which were immersed at 51°C. The results show further that weight losses occurred only in the composites that were immersed at 51 and 69°C. This loss is attributed to the leaching of rice hulls and water soluble products mainly lactic acid and probably low molecular weight oligomers from the composite during the degradation of PLA in water. The weight gains shown by all the products, which were immersed at 23°C, attests further the stability of PLA in water at mesophilic temperatures. On the contrary, the weight gain revealed by PLA that was immersed at 51°C may be explained by different phenomena. However, it is worthy to note that this product hardened while undergoing water absorption. This could be attributed to aging of the product and hydrolysis of the amorphous domains. As expected, the diffusion of water into the composites increased with the increase of rice hulls content. This agrees with the

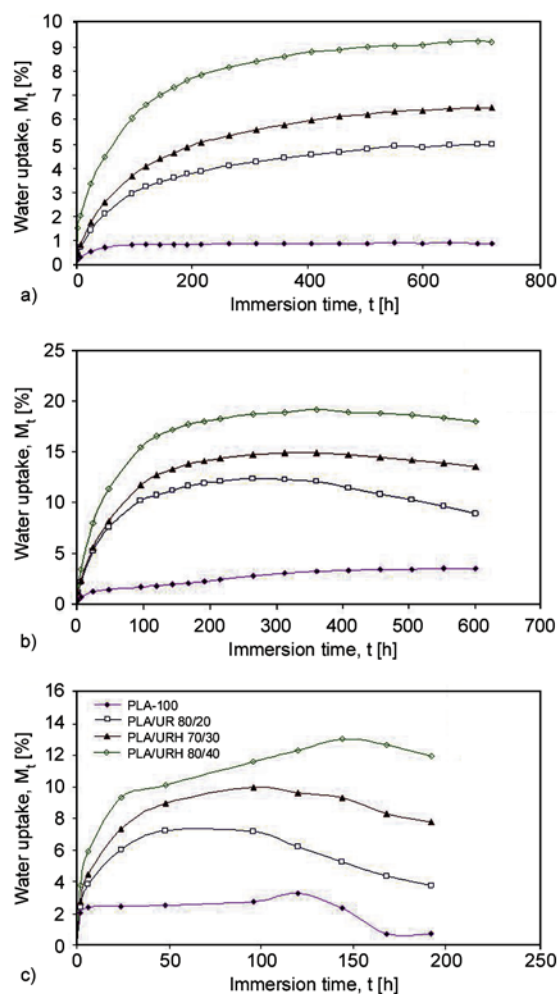


Figure 1. Moisture absorption in PLA/RH composites immersed in water at (a) 23°C, (b) 51°C and (c) 69°C

Table 1. Diffusion parameters of PLA and PLA/RH composites

Product	Temp [°C]	M _m [%]	D·10 ⁻⁵ [mm ² /s]	Weight gain of re-dried product [%]
PLA-100	23	0.87	0.665	-0.07
	51	3.57	0.223	-0.21
	69	—	—	3.16
PLA/URH 80/20	23	4.98	0.120	-3.15
	51	12.35	0.172	8.85
	69	7.19	1.676	12.10
PLA/URH 70/30	23	6.49	0.113	-0.25
	51	14.95	0.148	4.40
	69	9.96	1.164	10.31
PLA/URH 60/40	23	9.25	0.303	-1.46
	51	19.14	0.195	3.63
	69	1.00	—	9.89

previous studies [5,18] by demonstrating the role of rice hulls as hydrophilic fillers in the composite.

3.2. Thermal properties

The influence of hydrolytic degradations on the thermal properties of PLA/RH composites as measured by DSC1 system, are shown in Figure 2 and the summary is given in Table 2. As shown in Figure 2a, peaks ascribed to crystallization and melting of neat PLA did not appear during the re-heating cycle. Absence of the crystallization peak implies that the pellets were more amorphous. It is shown further that the crystallinity of PLA was slightly reduced during immersion of the PLA products in water at 23°C for 30 days. This is explained by a decrease of the crystallization and melting peaks

observed on the thermogram of this sample compared with the control PLA (PLA 100). The results show that the crystallization peaks of the composites were somewhat enhanced after addition of rice hulls in PLA (Figures 2b to 2d). These peaks increased considerably due to hydrolysis at higher temperatures. They were much stronger in the composites than in PLA at 51°C and increased substantially at 69°C in PLA as well as in the composites. The large melt crystallizations shown in these products are evidence of enormous transformation of amorphous PLA into crystalline phases as the polymer was undergoing hydrolysis in water at 51 and 69°C temperatures. The results also seem to suggest further that the presence of rice hulls somehow enhanced the crystallization of PLA during water

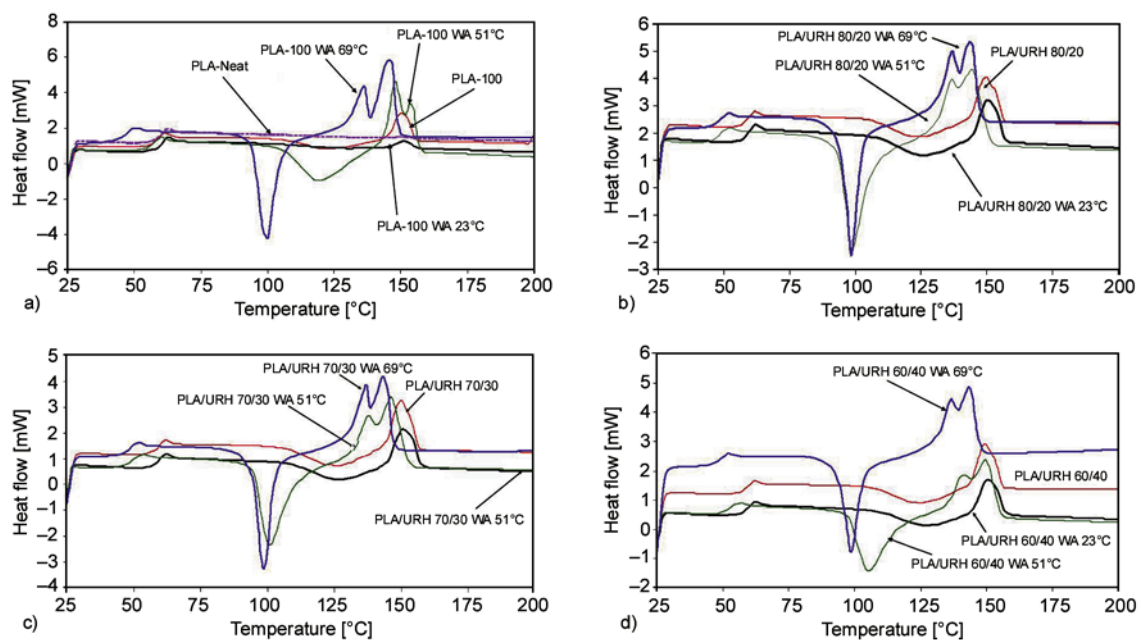


Figure 2. DSC thermograms of (a) PLA, (b) PLA/URH 80/20 composites, (c) PLA/URH 70/30 composites, and (d) PLA/URH 60/40 composites before and after water absorption

Table 2. Thermal properties of PLA/RH composites due to water absorption at different temperatures

Product	Immersion temp [°C]	T_g [°C]	T_c [°C]	T_m [°C]	ΔH_m [J/g]	χ_c [%]
PLA-100	–	59.0	122.5	150.0	8.6	6.4
	23	59.1	126.5	151.1	1.9	1.4
	51	56.2	119.6	148.0	26.1	19.3
	69	46.4	99.8	145.6	41.6	30.8
PLA/URH 80/20	–	57.9	123.4	149.3	10.6	6.3
	23	58.1	125.8	150.5	8.9	5.3
	51	49.0	99.0	144.6	29.9	17.7
	69	47.9	98.6	143.8	28.5	16.9
PLA/URH 70/30	–	58.1	125.1	149.4	11.7	6.1
	23	58.4	126.3	150.7	8.9	4.6
	51	48.8	101.4	146.4	27.8	14.4
	69	47.6	98.7	143.1	28.4	14.7
PLA/URH 60/40	–	58.4	124.1	149.4	9.0	4.0
	23	58.5	126.9	150.7	7.0	3.1
	51	51.7	105.3	149.5	19.6	8.7
	69	48.3	98.9	143.4	22.1	9.8

*Two fusion peaks observed in PLA and PLA/RH composites immersed at 51 and 69°C

absorption at 51°C. However, this may be subjected to further scrutiny. Intensities of the melting peaks also increased slightly at higher temperatures. However, two melting peaks were observed in the products that had been hydrolyzed in water at 51 and 69°C. Neither of these peaks could be associated with thermal transitions of rice hulls as this biomass does not melt or crystallize and also on the fact that two peaks appeared in PLA, which did not contain rice hulls. It is therefore permissible to associate these peaks to the melting of hydrolytic degradation products of PLA since they were only visible in the products that had been subjected to hydrolysis at higher temperatures.

The summary of DSC results presented in Table 2 show very small increase in the glass transition temperature (T_g) of PLA by 0.4°C at the immersion temperature of 23°C. This small increase could be associated with minor changes in the polymer that might have influenced a slight increase of its high molecular weight fractions. It is shown further that T_g , the crystallization temperatures (T_c) and melting temperatures (T_m) also decreased probably due to hydrolysis of the polymer at higher water temperatures. Kale *et al.* [16] applied Fox-Flory equation to demonstrate the reduction of the T_g with the decrease of the number average molecular weight (M_n) of commercial PLA products during degradation in a compost. Based on this relation, which has also been applied a couple of years earlier [22], we can associate the decrease of the T_g of PLA with the

reduction of its molecular weight due to hydrolysis. Perhaps there was a molecular weight degradation during water absorption that would be associated with the cleavage of the chain at –C–O– ester group by water molecules due to hydrolysis. To verify whether these changes are related to the molecular weight degradation of PLA or not, a molecular weight analysis was conducted by SEC. The results are shown in the corresponding section. Nevertheless, we cannot fully associate the physical changes of PLA products that were immersed at 23°C with any cross-linking or recombination reactions of the polymer under water at that temperature.

Change of crystallinity (χ_c) and fusion enthalpies (ΔH_m) due to hydrolysis of PLA were also examined. It is shown in Table 2 that the crystallinity and enthalpies of fusion of PLA decreased slightly at 23°C. However, it is shown further that there was a remarkable transformation of the amorphous region of PLA into crystalline phases at higher hydrolysis temperatures as shown by an increase of crystallinity. The largest transformation of the PLA to crystalline domains was achieved at 69°C, which was accompanied with maximum reduction of the T_g and T_m . Hydrolysis of the semi-crystalline PLA starts in the amorphous region transforming these domains to crystalline phases and it increases with the hydrolysis temperature [23]. The crystallinity can decrease if hydrolysis is extended in the crystalline domains once the hydrolysis of the amorphous region is over. The decrease of the T_g can be

related to molecular weight degradation as demonstrated previously using Fox-Flory equation [16]. It can thus be suggested that the development of crystalline phases in this polymer during hydrolysis at higher temperatures was accompanied with the reduction of its molecular weight. This proposition can also be verified by studying the molecular weight degradation of this polymer.

The representative results of the influence of hydrolytic degradations on the thermal stability of PLA and its composites as determined by TGA are shown at Figure 3. It is shown that all PLA products degraded in one major stage between 220 and 389°C. A secondary stage for the PLA/RH composites, which is shown between 370 and 530°C, was associated with the degradation of lignin and cellulose products in rice hulls. Additionally, there are two degradation stages between 220 and 333°C and from 333 to 389°C for the PLA product that was immersed at 69°C (PLA-100 WA69°C). These stages could be ascribed to thermal degradation of two hydrolytic degradation products of PLA with distinct thermal stabilities. Since these changes resulted from the hydrolysis of the polymer, it may be plausible to ascribe the two degradation stages to the decomposition of hydrolytic products with distinct molecular weights. By relating the decomposition temperature to the molecular weights as proposed by Kale *et al.* [16] using an expression similar to Fox-Flory equation, a higher molecular weight product decomposes at higher temperature and vice-versa. This implies that the first decomposition stage of this product could be attributed to the degradation of low molecular weight fractions of the polymer while the second stage involved hydrolytic degradation products with slightly higher molecular weight fractions. However, the legitimacy of this

assertion relies on the agreement with the molecular weight degradations results. It can also be shown further that peaks of maximum degradation zones for PLA and the composites that were immersed at 23°C generally occurred at higher temperatures. The high thermal stability of PLA was probably due to an increase of higher molecular weight fractions in the polymer during hydrolysis at this temperature. These products also lost large weights in the main degradation zones compared with similar products that were immersed at higher temperatures as indicated by stronger DTG curves peaks.

The influence hydrolytic degradations on the kinetics of thermal degradation of PLA were also studied using Horowitz and Metzger [24] model shown in Equation (4).

$$\ln \frac{1 - C^{1-n}}{1 - n} = \frac{E(\Delta T)}{RT_{\max}^2} \quad (4)$$

where $C = (w - w_f)/(w_0 - w_f)$ is the fraction of the sample lost, E is the activation energy, T_{\max} is the temperature at maximum weight loss obtained from the peaks of DTG curves, R is the universal gas constant, $\Delta T = T - T_{\max}$ and n is the order of reaction. The reaction orders, n , estimated from $C_{\max} = n^{1/(1-n)}$ were found to range from 0.6 to ~ 1.0 . The kinetics of thermal degradation of PLA was approximated using the first order reaction of this model. The left term of Equation (4) was reduced to $\ln[\ln \alpha]$ and E was obtained from the slope of the linear relation $\ln[\ln(w_0 - w_f)/(w - w_f)]$ versus ΔT . The results shown in Table 3 suggest that the thermal stability of PLA was slightly reduced due to processing. After hydrolysis of PLA in water at higher temperatures, the activation energy of thermal degradation generally decreased except at the immersion temperature of 23°C, where it slightly increased. In

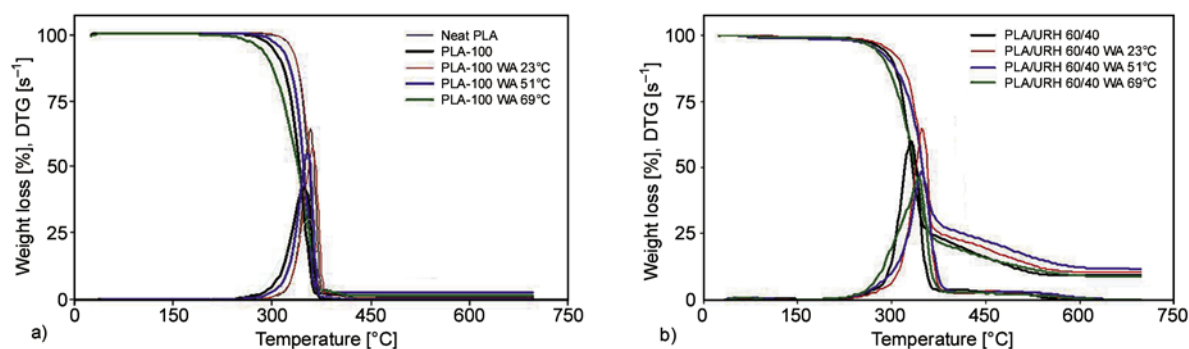


Figure 3. Thermograms of (a) PLA and (b) PLA/URH 60/40 composites products before and after water absorption at different temperatures

Table 3. Kinetic parameters of thermal and hydrolytic degradation of PLA and its rice hulls composites

Product	Decomposition step [°C]		T_{\max} [K]		E [kJ/mol]		Estimated reaction order, n	
PLA-Neat	291–375		357.5		332.5		1.2	
PLA-100 (control)	266–371		350.5		224.0		0.6	
PLA-100WA23°C	291–375		361.0		305.8		1.0	
PLA-100WA51°C	266–371		354.0		250.7		0.7	
PLA-100WA69°C	231–378		357.5		161.6		overall	
PLA-100WA69°C	231–336	336–378	326	357.5	170.0	359.9	0.4	1.9

conjunction with SEC results, it may be possible to explain clearly and relate the changes to the molecular weight of the polymer. However, with the fact that higher molecular weight products require more energy to decompose and vice versa, the decrease in the activation energy can be related to molecular weight degradations. Concurrently, a slight increase in the activation energy observed at 23°C attests the proposition of the increase of high molecular weight fractions in the polymer at this temperature.

3.3. Infrared spectroscopy analysis

The results of infrared spectroscopy of PLA and PLA/RH composites, which were subjected to

water absorption at 23, 51 and 69°C, are shown in Figures 4a to 4d. In this analysis the region of interest is between 1800 and 800 cm^{-1} where active ester and methyl groups of PLA are located. The results show strong absorption between ~ 1747 and $\sim 1080 \text{ cm}^{-1}$, which is ascribed to symmetrical stretching of C=O and –C–O– groups of ester bonds, respectively. Unexpectedly, the vibration of rice hulls functional groups (Si, OH and C=C, etc) could not be shown on the spectra suggesting that the rice hulls might have been completely dispersed into the matrix and therefore were not available for surface spectroscopic analysis. Hydrolysis due to hydrogen bonding or nucleophilic attack by water molecules

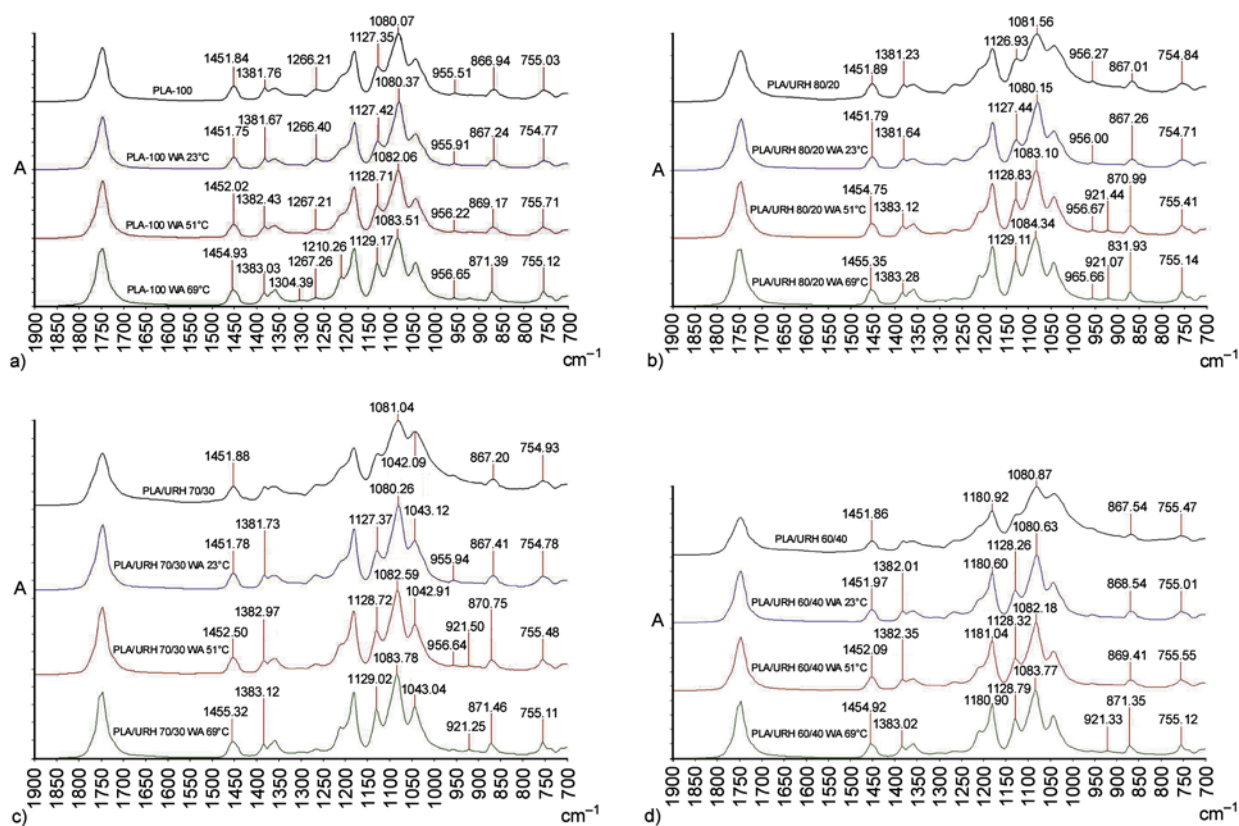


Figure 4. a) Infrared spectra of PLA products due to hydrolysis at different temperatures, b) Infrared spectra of PLA/URH 80/20 composites due to hydrolysis at different temperatures, c) Infrared spectra of PLA/URH 70/30 composites due to hydrolysis at different temperatures, d) Infrared spectra of PLA/URH 60/40 composites due to hydrolysis at different temperatures

at the –C–O– ester bond tends to shift ester bands to lower frequencies. The results show that the carbonyl group C=O band ascribed to ester bond did not shift. The only notable change shown on this band is a slight increase in intensity by 1.03, 1.23 and 1.14 relative to control PLA products. This change may be associated with stretching vibration that favored the hydrolysis of the polymer chains. Although a fraction of MA was used as a grafting agent between the polymer and the rice hulls, its presence could not be detected by an infrared spectroscopy in the composites between 1700 and 1600 cm^{-1} . This could be attributed to inadequate dispersion of the little proportion of MA used in the preparation of the PLA/RH composites.

Further changes in the structure of PLA due to hydrolysis and water absorption were noted in the regions of 1451–1454 cm^{-1} , 1381–1383 cm^{-1} , 1264–1267 cm^{-1} , 1210 cm^{-1} , 1180–1181 cm^{-1} , 1127–1129 cm^{-1} , 1080–1083 cm^{-1} , 955–956 cm^{-1} , 921 cm^{-1} absorptions. The 1451 cm^{-1} band, which is attributed to asymmetric stretching of methyl –CH₃ group, shifted slightly to higher frequency by 3 cm^{-1} at higher hydrolysis temperatures. This is associated with changes of the hydrophobic properties of the PLA, which is conferred by the –CH₃ group, during hydrolysis. The band at 1375 cm^{-1} assigned to symmetric deformation of methyl –CH₃ group occurred at 1381 cm^{-1} and also shifted slightly to higher frequencies by 2 cm^{-1} with the increase of hydrolysis temperatures. A similar trend associated with this group can be observed at ~1264 cm^{-1} . However, their intensities decreased slightly at higher water absorption temperatures. The 1080 cm^{-1} ascribed to symmetric stretching of –C–O– band of ester groups also shifted slightly to higher frequencies by 3 or 4 cm^{-1} due to hydrolysis at higher temperatures. This change can be attributed to strengthening of the ester bond against hydrolysis.

3.4. Molecular weight degradation analysis

Table 4 shows the results of molecular weights (\overline{M}_w , \overline{M}_n) analysis of PLA that had been subjected to water absorptions at 23, 51 and 69°C. It is shown that the weight average molecular weight (\overline{M}_w) and the number average molecular weight (\overline{M}_n) of control PLA were around 153.1 and 93.9 kDa, respectively. After 30 days of water absorption at 23°C,

Table 4. Molecular weights degradation of PLA due to water absorption at different temperatures

Product	Temperature [°C]	\overline{M}_w [kDa]	\overline{M}_n [kDa]	$\overline{M}_w/\overline{M}_n$
PLA-100 (control)	–	153.13	93.89	1.631
PLA-100WA23°C	23	156.89	82.80	1.895
PLA-100WA51°C	51	42.12	20.38	2.067
*PLA-100WA69°C	69	10.70	5.31	2.016
	Low MW peak	4.62	3.14	1.471

*Two peaks observed

increased slightly by 3.8 kDa while $\overline{M}_w/\overline{M}_n$ also increased. The increase of $\overline{M}_w/\overline{M}_n$ implies that the molecular weight distribution was broadened due to the increase of high molecular weight fractions. Hydrolysis and cleavage of ester bonds of PLA is said to occur randomly where longer chains of the polymer become more susceptible to cleavage than the shorter chains [16]. The reduction in \overline{M}_n observed with a subsequent increase of \overline{M}_w could be ascribed to partial cleavage of some high molecular weight chains and recombination reactions leading to addition of high molecular weight fractions in the polymer. Kale *et al.* [17] ascribed a similar change during their study on composting of commercial PLA products to the cross-linking or recombination reactions. However, we cannot ascertain if there was any cross-linking reaction in these products at this condition. It is shown further that as the polymer was subjected to hydrolysis at higher temperatures, both \overline{M}_w and \overline{M}_n decreased significantly. This was attributed to an increase of low molecular fragments in the polymer with subsequent broadening of molecular distributions as shown by an increase of $\overline{M}_w/\overline{M}_n$. This change was associated with more hydrolysis of ester bonds and more cleavage of the chains as the polymer was heated in water at higher temperatures. The cleavage was more significant at 69°C where the \overline{M}_w of the polymer was reduced to 10.7 kDa in less than 9 days compared to 42.1 kDa at 51°C in 25 days. Despite exhibiting abnormal hardness and slight increase in the weight after re-drying, the PLA that was immersed at 51°C only showed the reduction of molecular weights and broadening of the molecular weight distribution peak. These changes are also related to the cleavage of the molecular weight chains with subsequent increase of low molecular weight fractions in the polymer.

3.5. Morphological analysis

SEM results for the morphological analysis of fracture surfaces of PLA and PLA/RH composites after water absorption at 23, 51 and 69°C are shown in Figures 5–8. It can be shown in Figures 5a to 5b that PLA was not substantially affected physically during water absorption at 23 and 51°C for 30 and 25 days, respectively. However, this polymer was seriously deteriorated and shattered only in 9 days after being subjected to hydrolysis in water at 69°C. This is explained by random shattering of the polymer matrix as shown in Figure 5c, which indicates that the polymer was fragile. It is shown further that the deterioration of the matrix in the composites was influenced by the immersion temperature as well as the contents of rice hulls. At 23°C, the matrix did not indicate any physical deterioration as shown on the fracture surface. Fractures in these products were due to breaking of the rice hulls (RH) and the

matrix (M) or due to partial debonding (Figures 6 to 8). However, significant development of embrittlement in the polymer matrix (M) especially at higher immersion temperatures was observed. The matrix was made fragile while most of the rice hulls (RH) remained intact as shown in Figures 6b and 6c, 7b and 7c, and 8b and 8c. Figures 9a and 9b suggest that the rice hulls in some way enhanced the deterioration of the matrix. This is shown by the develop-

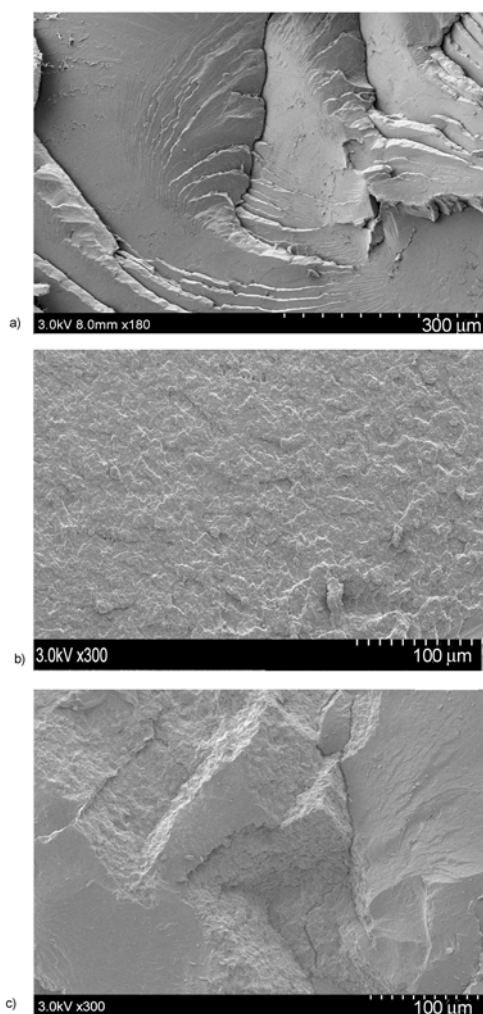


Figure 5. SEM image of the fracture surface of PLA after water absorption at (a) 23°C-30 days, (b) 51°C-25 days and (c) 69°C-9 days

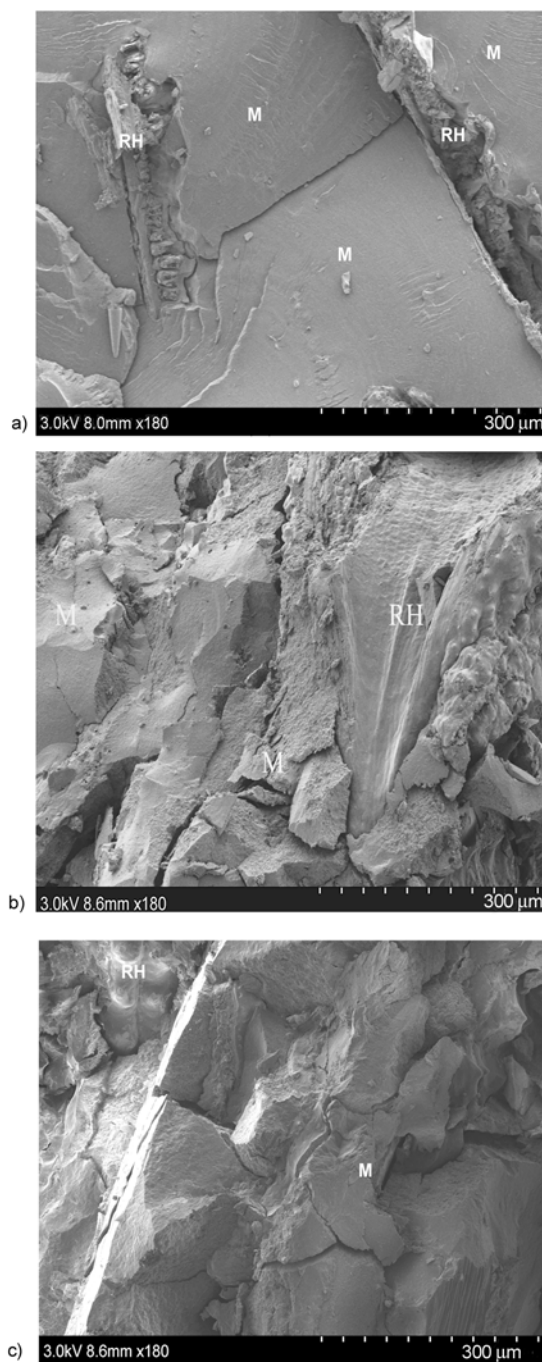


Figure 6. SEM image of the fracture surface of PLA/URH 80/20 composite after water absorption at (a) 23°C-30 days, (b) 51°C-25 days and (c) 69°C-9 days

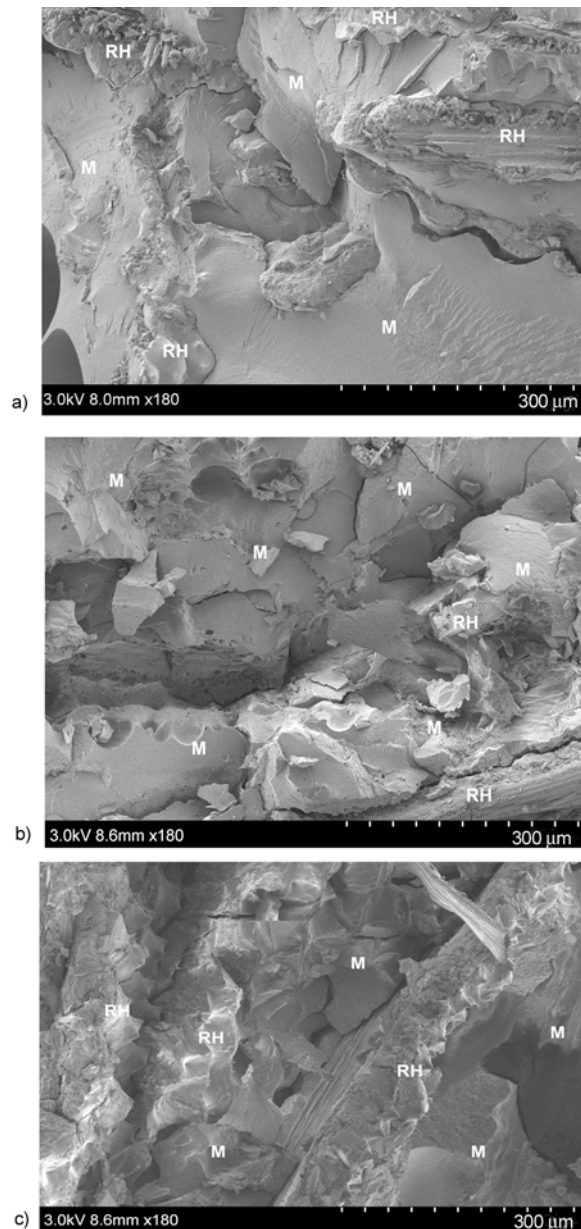


Figure 7. SEM image of the fracture surface of PLA/URH 70/30 composite after water absorption at (a) 23°C-30 days, (b) 51°C-25 days and (c) 69°C-9 days

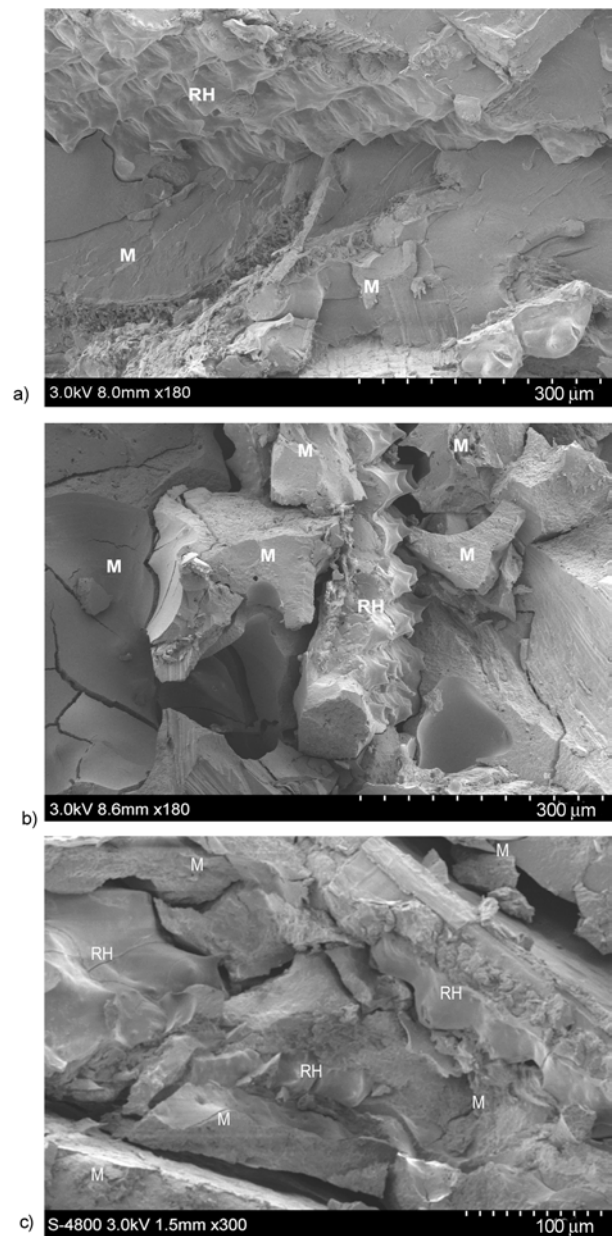


Figure 8. SEM image of the fracture surface of PLA/URH 60/40 composite after water absorption at (a) 23°C-30 days, (b) 51°C-25 days and (c) 69°C-9 days

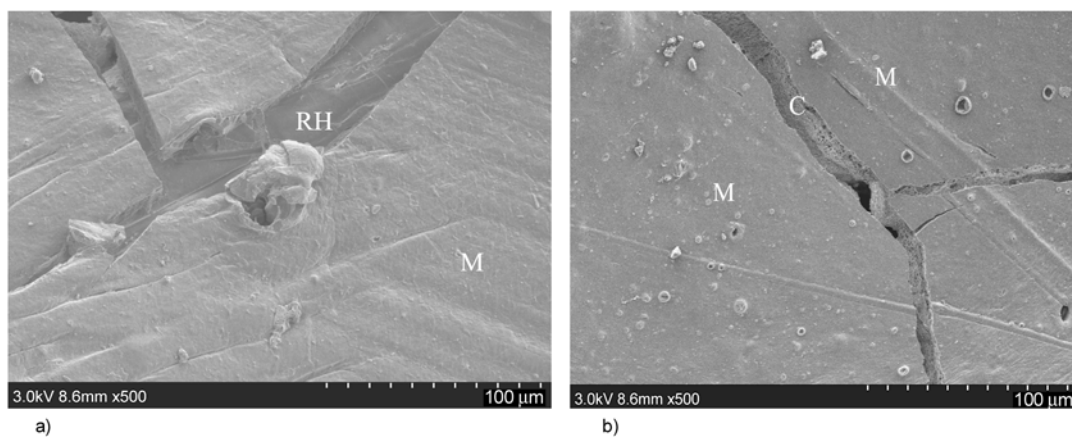


Figure 9. Surface of (a) PLA/URH 60/40 and (b) PLA/URH 70/30 composites after water absorption at 51°C-25 days

ment of cracks (C) on the surface of the composite, which were most probably attributed to the swelling of the rice hulls (RH) as shown in Figure 9a. It might have been the swelling of the rice hulls during water absorption that accelerated the fragmentation of the weakened matrix.

4. Conclusions

Degradation of PLA and PLA/RH composites due to hydrolysis in water was influenced significantly by the temperature of water. At the mesophilic temperature $\sim 23^\circ\text{C}$, these products were fairly stable. They absorbed between 0.87 and 9.2% water in 30 days with no appreciable physical and chemical changes as revealed by SEM, infrared spectroscopy and SEC, respectively. However, close to the glass transition temperature (T_g) of PLA at 51°C , PLA started to show remarkable physical and chemical deteriorations. The rate of water diffusion and degradation in the composites increased significantly above the T_g (69°C) leading to saturation in less than 9 days. This was accompanied with the development of fragility in the material as revealed by SEM and an increase in crystallinity by 24%. The T_g also reduced significantly by 13°C whereas the average molecular weight of the polymer decreased to $\sim 42\,100$ and $\sim 10\,700$ Da at 51 and 69°C , respectively. These changes were associated with the hydrolytic degradation of PLA. Rice hulls in some way enhanced indirectly the disintegration of the matrix during their water absorption and swelling as was suggested by SEM. The degradation of PLA due to hydrolysis in water was also demonstrated by the reduction of the thermal stability of its products.

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