

Synthesis and Characterization of Chemically-Modified Cassava Starch Grafted with Poly(2-Ethylhexyl Acrylate) for Blending with Poly(Lactic Acid)

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Native cassava starch (CS) is chemically modified by grafting with 2-ethylhexyl acrylate (EHA) monomer to make it more hydrophobic for improved blending with poly(lactic acid) (PLA). Grafting is carried out using CS:EHA weight ratios of 2:1, 1:1, 1:2, and 1:3 in a methanol-water solvent mixture at 45 °C for 48 h. L-Ascorbic acid and hydrogen peroxide are used as the redox initiating system. Following purification, the poly(2-ethylhexyl acrylate)-grafted starch, starch-g-PEHA, is obtained either as a finely divided powder or as a slightly tacky solid with % grafting values in the range of 13–26% by weight. The main objective of this chemical modification is to improve the interfacial adhesion between the starch particles and the PLA matrix through the hydrophobic PLA-PEHA interactions. PLA/starch-g-PEHA blends are prepared in the form of solution-cast films with weight ratios ranging from 100/0 to 60/40. Tensile testing of the films shows a marked increase in extensibility and toughness up to a loading of 10% starch-g-PEHA above which the properties deteriorated rapidly due to starch particle aggregation. Thus, for potential use as biodegradable film packaging, the best properties are obtained for the PLA/starch-g-PEHA 90/10 blend.

1. Introduction

Among the synthetic biodegradable polymers, poly(lactic acid), PLA, has been the focus of much attention because it is produced from renewable resources, is biodegradable and compostable, exhibits mechanical properties comparable with many commercial polymers, and can be melt processed using conventional thermoplastic processing equipment. Consequently, there is now a great deal of information available in the literature on PLA and its properties, modifications, and applications.^[1–10]

In contrast, PLA also has some notable disadvantages such as its low heat deflection temperature, brittleness in certain applications, slow rate of crystallization, inferior water vapor and gas barrier properties, and its relatively high cost compared with commodity plastics. Therefore, in order to diversify PLA's range of applications, there is increasing interest nowadays in how its properties can be

modified by, for example: (1) the use of additives such as nucleating agents, plasticizers, and impact modifiers; (2) blending with other polymers; and (3) nanocomposites with inorganic materials such as clay, zinc oxide, titanium dioxide, and carbon nanotubes.^[1–6] However, even when its properties can be improved, PLA's relatively high cost still limits its competitiveness in the marketplace.


One way in which the unit cost of PLA can be reduced is by blending it with a naturally abundant biopolymer such as starch, especially for use in applications that do not require high performance such as biodegradable plastic bags and food packaging.^[11–13] In addition to lowering the cost, starch also increases the rate of PLA biodegradation due to its hydrophilicity. However, blending hydrophobic PLA with hydrophilic starch also has its downside. PLA and starch are thermodynamically immiscible which results in phase separation and poor interfacial adhesion between the PLA matrix and the starch particles. Furthermore, starch does not melt and its moisture sensitivity can cause hydrolytic degradation of PLA to occur at the high temperatures used during melt processing. Consequently, it is found in practice that the dry native starch concentration at which useful materials can be prepared is

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limited to approximately 10% by weight beyond which the mechanical properties, in particular tensile strength, start to decrease dramatically.

In order to improve its melt processability, native starch can be gelatinized to give thermoplastic starch (TPS) which is a rubbery material obtained by adding plasticizers such as water and glycerol to break down the hydrogen bonding in the starch particles. The amount of glycerol incorporated in TPS is usually in the range of 25–30% by weight and controls the viscosity of the TPS in the melt phase and its rigidity in the solid form. Even though it has been reported that TPS in PLA/TPS blends can improve processability and the TPS phase can be deformed and dispersed to a much finer state than dry native starch, problems still remain with TPS such as its moisture sensitivity, low temperature resistance, plasticizer migration, and starch recrystallization over time leading to embrittlement.^[14] Nevertheless, PLA/TPS blends and their various modifications have attracted a great deal of interest and been widely reported in the literature.^[15–18]

As an alternative to plasticization, coupling agents such as maleic anhydride and methylene diphenyl diisocyanate (MDI) have also been used in an attempt to improve interfacial adhesion. Blends with MDI had enhanced mechanical properties that could be explained by the reaction of the isocyanate ($-N=C=O$) groups with the OH groups of both the starch and the PLA chain-ends, thereby covalently linking the starch to the PLA.^[19–21] However, the effect was heavily dependent on the distribution of the MDI and was lessened by its preferred reaction with any water present in the starch.

Notwithstanding these various developments, promising results in recent years have been obtained by chemical modification of the starch by graft copolymerization with a wide range of different monomers and polymers. This approach has recently been the subject of a comprehensive review.^[22] Again the main objective has been to improve interfacial adhesion but in this case by functionalizing the starch with a grafted polymer or copolymer which is more compatible with the PLA matrix. There are two strategies for achieving this: (1) the “grafting from” approach in which the grafting monomer is polymerized directly from the starch main chain and (2) the “grafting onto” approach in which a chain-end functionalized polymer is grafted onto the starch main chain. The various monomers and polymers which have been grafted via these methods include: (monomers) styrene, acrylic acid, vinyl acetate and methyl methacrylate; and (polymers) poly(vinyl alcohol), poly(ethylene glycol), poly(methyl methacrylate), and polyacrylamide: others are listed in the recent review^[22] and also in an earlier review.^[23]

This present paper now describes the chemical modification of native cassava starch by the “grafting from” approach using 2-ethylhexyl acrylate (EHA) as the grafting monomer. There have been previous reports of EHA being graft-polymerized from allyl starch^[24] and gelatin films^[25] but none, as far as we are aware, from unmodified native starch. Structurally, EHA was chosen on the basis of its easy polymerizability through the acrylate group and its large hydrophobic component in the form of the 2-ethylhexyl group. It was also chosen with cost effectiveness in mind as it is relatively inexpensive. EHA is one of the major base monomers used in the industrial production of pressure-sensitive acrylate adhesives. Therefore, as poly(2-ethylhexyl acrylate) (PEHA) is known to be an inherently soft and tacky material, it raised the interesting prospect that PEHA-grafted chains could have an interfacial adhesive effect in a PLA/starch-g-PEHA blend. This paper now sets out to describe the synthesis and characterization of starch-g-PEHA, its blending with PLA, how the prospect that it could improve the properties of PLA films was investigated, and to what extent this improvement has been achieved.

2. Experimental Section

2.1. Materials

Native cassava starch (approx. 12% by wt. moisture content, average particle size = 13.6 μm) was obtained from Eiamheng Cassava Starch Industry Co., Ltd., Nakhon Ratchasima, Thailand, in powder form and was vacuum dried at 80 °C to constant weight before use. When dry, native Thai cassava starch typically consists of approximately 80% amylopectin, 17% amylose, and 3% other constituents such as proteins, lipids, and crude fibers.^[26]

PLA in pellet form was also a commercial product, Ingeo™ Biopolymer 2003D (NatureWorks®) for use in food packaging, and was vacuum dried at 40 °C for 24 h before use. It had a viscosity-average molecular weight M_v of $1.46 \times 10^5 \text{ g mol}^{-1}$, as determined by dilute-solution viscometry using chloroform as the solvent at 30 °C. The M_v value was calculated from the Mark-Houwink equation: $[\eta] = 1.31 \times 10^{-4} M_v^{0.759} \text{ dl/g}$.^[27]

2-Ethylhexyl acrylate (Acros Organics, 99%, stabilized) (EHA) was shaken successively with equal volumes of 10% w/v aqueous sodium hydroxide solution and then distilled water in order to remove the stabilizer before being dried over anhydrous sodium sulfate.

The chemical structures of the main anhydroglucose repeat unit in cassava starch, PLA and the EHA monomer are shown in **Figure 1**.

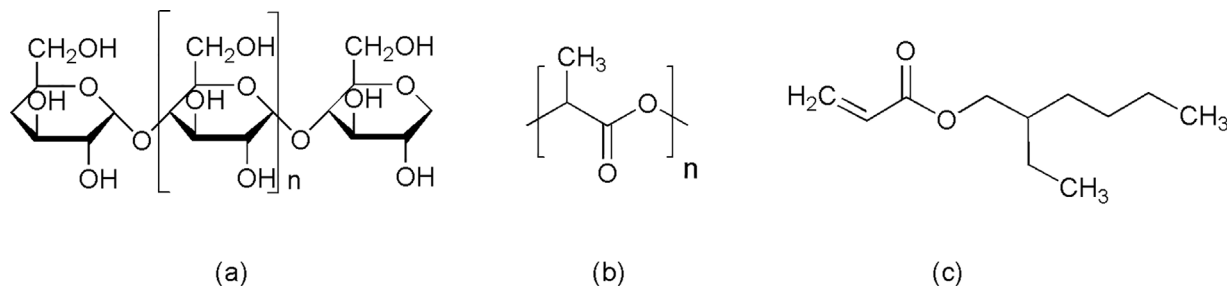


Figure 1. Chemical structures of a) the anhydroglucose repeat unit of starch, b) the PLA repeat unit, and c) the EHA monomer

2.2. Instrumental Methods

Polymer molecular weight determination of PLA was carried out by dilute-solution viscometry using a Schott-Geräte AVS300 Automatic Viscosity Measuring System with chloroform as the solvent at 30 °C.

¹H-NMR microstructural analysis was carried out using a Bruker Avance DRX-400 Nuclear Magnetic Resonance Spectrometer operating at a field frequency of 400 MHz. Deuterated chloroform (CDCl₃) was used as the solvent for PEHA at room temperature (23 °C) and deuterated dimethyl sulfoxide (d₆-DMSO) for starch and starch-g-PEHA at 100 °C. Tetramethylsilane (TMS) was the internal standard.

Thermal analysis for determining glass, (cold) crystallization and melting transition temperatures (T_g , T_c , T_m) and initial thermal decomposition temperature (T_d) was carried out using a Perkin-Elmer DSC7 Differential Scanning Calorimeter (0 → 200 °C, heating rate 10 °C min⁻¹) and a Perkin-Elmer TGA7 Thermogravimetric Analyzer (50 → 550 °C, heating rate 20 °C min⁻¹) respectively.

Percent light transmittance (%T) of thin films as a measure of optical clarity was measured using a Molecular Devices SpectraMax[®] M2 UV-Visible Multimode Microplate Reader at a wavelength of 500 nm with air as the reference. Measurements were taken from at least three different film samples and five different areas of each film and averaged in accordance with the ASTM D1746-15 test method for transparency of plastic sheeting.^[28]

Water contact angle measurements of surface hydrophilicity were performed on thin films by the sessile drop method using a GBX Digidrop Contact Angle Meter. Measurements were carried out with drops of 2.0 ± 0.3 μL volume and repeated at least 10 times at different positions on the sample and the results averaged. As the contact angle is extremely sensitive to contamination, the sample surfaces were cleaned with ethanol and water and patted dry prior to measurement.

Tensile testing of thin films (thickness 0.065 ± 0.005 mm) was performed using a Lloyds LRX+ Universal Testing Machine in accordance with the ASTM D882-02 test method for thin plastic sheeting.^[29] Test specimens were pre-conditioned at 23 ± 2 °C and 50 ± 5% relative humidity for 48 h prior to testing. At least five rectangular-shaped specimens (12 × 1 cm) were tested from each of three film samples (gauge length 10 cm, crosshead speed 5 cm min⁻¹) and the derived parameters from the stress-elongation curves averaged.

For SEM analysis of fracture surfaces, specimens were mounted on stainless steel stubs with a conductive carbon tape, gold-coated, and then imaged using a JEOL JSM 5910LV Scanning Electron Microscope operating at an accelerating voltage of 15 kV at 23 °C.

2.3. Preparation of Starch-g-Poly(2-Ethylhexyl Acrylate), Starch-g-PEHA

The procedure and conditions used for the preparation of starch-g-PEHA were similar to those described in an earlier report on the graft copolymerization of methyl methacrylate (MMA) from a lignocellulosic fiber.^[30] A total of 5.00 g of pre-dried native

cassava starch were stirred in 50 mL of distilled water for 24 h at room temperature in a 500 mL round-bottomed flask to swell the starch particles and to activate the methylol (–CH₂OH) sites for grafting. 0.28 g (0.0016 mol) of L-ascorbic acid and 1.37 g of 30% w/w hydrogen peroxide in water (0.41 g H₂O₂ = 0.012 mol) were then added as the redox initiating system. As 2-ethylhexyl acrylate (EHA) monomer has negligible solubility in water (0.01 wt% at 20 °C) but is soluble in alcohols, 200 mL of a water:methanol 1:4 v/v mixture were then added followed by 5.00 g (0.027 mol) of EHA to give a starch:EHA w/w ratio of 1:1. Graft copolymerization was then carried out with the reaction flask immersed in a water bath at 45 °C for 48 h with constant magnetic stirring. The temperature of 45 °C was chosen so that the starch would swell but not gelatinize.

At the end of the reaction period, the starch-g-PEHA product was filtered off under vacuum in a sintered glass filter of porosity #3 and purified by extraction with chloroform to remove any PEHA homopolymer and unreacted EHA monomer. Finally, the starch-g-PEHA was re-filtered, washed with methanol, and dried to constant weight in a vacuum oven at 45 °C for 48 h. The final starch-g-PEHA product was obtained as a finely-divided white powder in 60% yield. This procedure was then repeated using starch:EHA w/w ratios of 1:0.5, 1:2, and 1:3.

The main initiation and propagation reactions taking place during the graft copolymerization are shown in **Figure 2**. While termination reactions (not shown) can occur by radical combination, disproportionation, and chain transfer, combination is considered to be the most likely termination mechanism.^[22,30] As shown in reaction (d), this is a “grafting from” type reaction in which the EHA monomer is polymerized from radicals generated on the starch. However, as shown in reaction (e), competing EHA homopolymerization also occurs by HO• radical initiation. The competitiveness between grafting and homopolymerization depends on the relative reactivities and concentrations of the starch-CH₂O• and HO• radicals in reactions (d) and (e) which generally tend to favor homopolymerization.

2.4. Solvent Blending and Film Preparation

Although the starch-g-PEHA products could neither melt nor dissolve in common organic solvents at room temperature, solvent blending was the preferred method as it appeared to give a greater uniformity of dispersion of the starch-g-PEHA particles in the PLA solution. For the same reason, the starch-g-PEHA 1:1 w/w product (**Table 1**) was chosen for this study as it was obtained as a finely-divided powder rather than as an agglomerated, slightly tacky solid.

Prior to blending, both the PLA pellets and the starch-g-PEHA were rigorously dried in a vacuum oven at 50 °C for 24 h in order to remove any adsorbed moisture. They were then blended by stirring in chloroform as the solvent in PLA:starch-g-PEHA w/w ratios of 100:0, 90:10, 80:20, 70:30, and 60:40. The concentration of each solvent blend was 0.6 g/30 mL. Each solution was poured into a Petri dish of 12 cm diameter, left overnight for the solvent to evaporate slowly and the drying process then completed in a vacuum oven at 45 °C for 8 h to remove the final traces of solvent. The film thickness obtained was in the range of 0.065 ± 0.005 mm as measured with a micrometer.

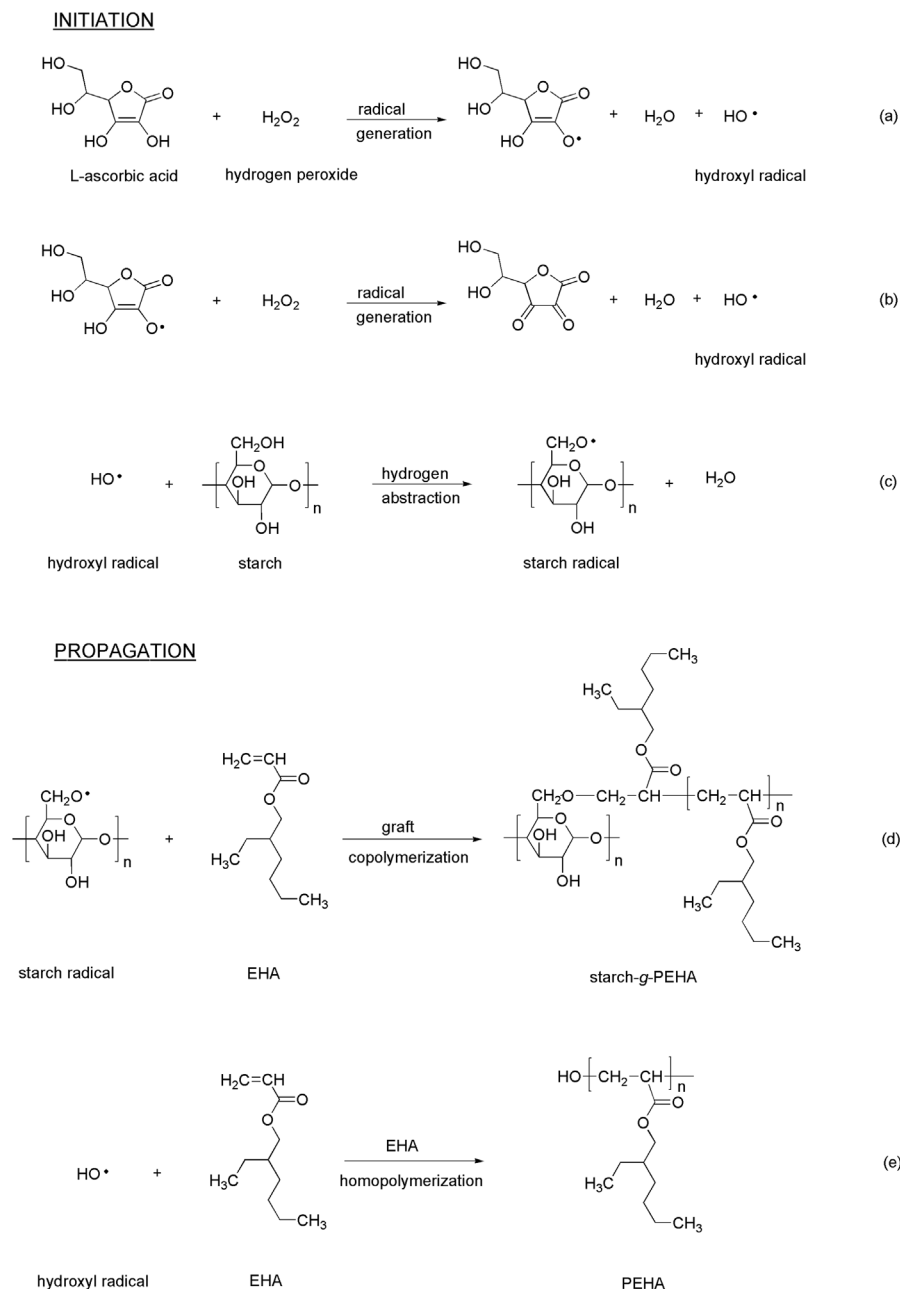


Figure 2. Mechanism of starch-g-PEHA graft copolymerization showing the main initiation and propagation reactions involved.

3. Results and Discussion

3.1. Starch-g-PEHA Copolymer Characterization

3.1.1. Physical Properties

The % conversion, % grafting, % grafting efficiency, and physical appearance of each of the starch-g-PEHA products are summarized in Table 1. The values were calculated from the following equations.

$$\% \text{ Conversion} = \frac{W_2}{W_1} \times 100\% \quad (1)$$

$$\% \text{ Grafting} = \frac{W_2 - W_3}{W_3} \times 100\% \quad (2)$$

$$\% \text{ Grafting efficiency} = \frac{W_2 - W_3}{W_4} \times 100\% \quad (3)$$

where W_1 = combined initial weights of native starch and EHA monomer, W_2 = final weight of purified starch-g-PEHA,

Table 1. % Conversion, % grafting, % grafting efficiency, and physical appearance of each of the purified starch-g-PEHA products prepared from different initial starch:EHA w/w ratios.

Starch:EHA (w/w)	Conversion (%)	Grafting (%)	Grafting efficiency (%)	Physical appearance of starch-g-PEHA
1: 0.5	75	13	25	Particles similar to original starch
1: 1	60	20	20	Finely-divided white powder
1: 2	45	34	17	Agglomerated, slightly tacky solid
1: 3	34	36	12	Agglomerated, slightly tacky solid

W_3 = initial weight of native starch, W_4 = initial weight of EHA monomer.

As the results in Table 1 show, increasing the amount of EHA relative to starch increased the % grafting but decreased the overall % conversion and % grafting efficiency. With grafting efficiencies of 25% or less, these results indicate that most of the EHA either underwent homopolymerization or remained unreacted. As mentioned previously, the preference for homopolymerization over grafting can be attributed to the lower reactivity of the starch- $\text{CH}_2\text{O}^\bullet$ radical compared to the OH^\bullet radical (Figure 2) together with the fact that the starch particles, unlike the EHA monomer, were not in solution. These results in Table 1 are similar to those reported for the preparation of starch-g-poly(methyl methacrylate) using potassium persulfate as the redox initiator.^[31]

It was also important to note the change in physical appearance as the % grafting increased. Whereas the starch-g-PEHA product from starch:EHA 1:1 with a % grafting of 20% was a finely-divided, non-adhering powder, the 1:2 and 1:3 products with % graftings of 35 and 36% were agglomerated, slightly tacky solids due to the adhesive nature of PEHA. This agglomeration and tackiness tended to hinder the dispersability of the starch-g-PEHA during the solvent blending process which was the reason why the more powdery 1:1 product was chosen for blending with PLA.

3.1.2. Structural Characterization by $^1\text{H-NMR}$ Spectroscopy

The $^1\text{H-NMR}$ spectra of the starch, PEHA homopolymer, and starch-g-PEHA graft copolymer are shown in Figures 3, 4 and 5 respectively. Whereas the PEHA $^1\text{H-NMR}$ spectrum could be recorded in deuterated chloroform (CDCl_3) as solvent at room temperature, the starch and starch-g-PEHA spectra had to be recorded in deuterated dimethyl sulfoxide (d_6 -DMSO) at 100°C in order to keep the samples in solution. When compared with the starch and PEHA spectra as references, the starch-g-PEHA spectrum in Figure 5 shows peaks specific to g-PEHA in the δ 0.8–2.4 ppm range. As the starch-g-PEHA sample in Figure 5 had a % grafting of only 20% (Table 1), the g-PEHA peaks are relatively small compared with the starch peaks.

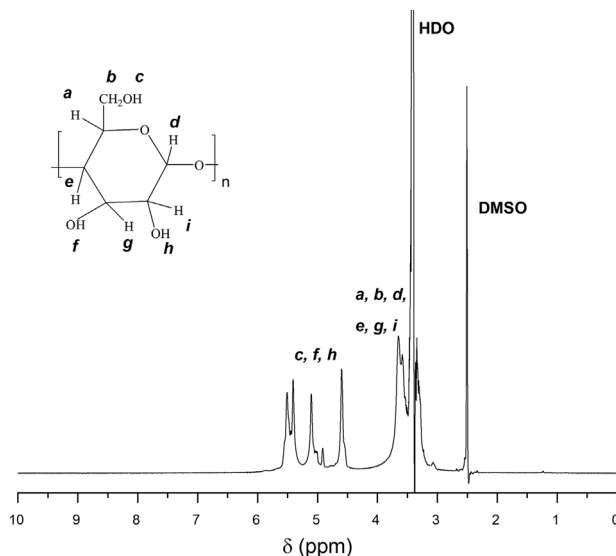


Figure 3. 400 MHz $^1\text{H-NMR}$ spectrum of native cassava starch recorded in d_6 -DMSO as solvent at 100°C .

3.2. PLA/Starch-g-PEHA Blended Films

3.2.1. Thermal Analysis (DSC and TGA)

The DSC thermograms of the PLA/starch-g-PEHA blended films are compared in Figure 6. The thermograms were recorded as second heating scans from $0 \rightarrow 200^\circ\text{C}$ at a heating rate of $10^\circ\text{C min}^{-1}$ following cooling from the melt at $10^\circ\text{C min}^{-1}$ to ensure that the thermal histories of the samples were all identical. The various transition temperatures (T_g , T_c , T_m), heats of crystallization and melting (ΔH_c , ΔH_m) and initial (X_i) and final (pre-melt) (X_f) % crystallinities are summarized in Table 2.

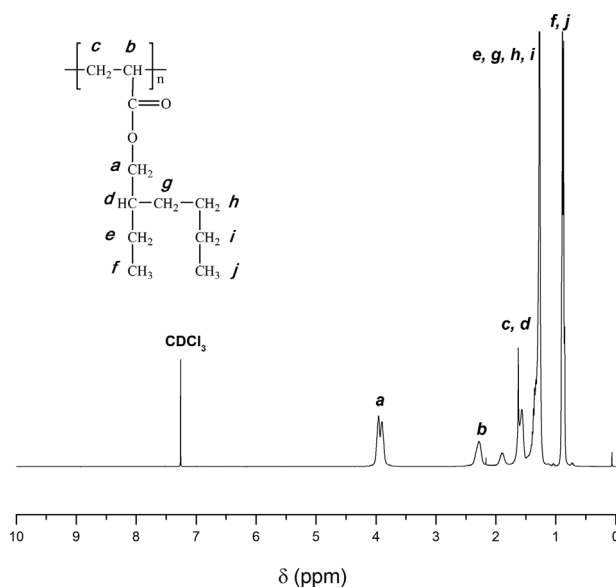


Figure 4. 400 MHz $^1\text{H-NMR}$ spectrum of PEHA recorded in CDCl_3 as solvent at room temperature.

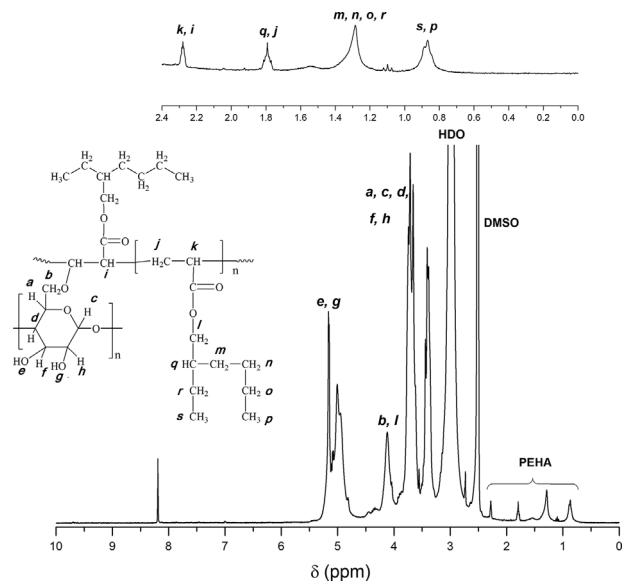


Figure 5. 400 MHz $^1\text{H-NMR}$ spectrum of starch-*g*-PEHA recorded in d_6 -DMSO as solvent at 100°C .

The values of X_i and X_f were calculated from the equations:

$$\text{Initial \% crystallinity} = X_i = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^* \times w_{\text{PLA}}} \times 100\% \quad (4)$$

$$\begin{aligned} \text{Final (pre-melt) \% crystallinity} &= X_f \\ &= \frac{\Delta H_m}{\Delta H_m^* \times w_{\text{PLA}}} \times 100\% \end{aligned} \quad (5)$$

where ΔH_m = heat of melting (J g^{-1}) \propto area under the twin PLA melting peaks, ΔH_c = heat of crystallization (J g^{-1}) \propto area under the crystallization peak, ΔH_m^* = heat of melting of a 100% crystalline sample = 93.7 J g^{-1} for PLA,^[32] w_{PLA} = weight fraction of PLA in the blend.

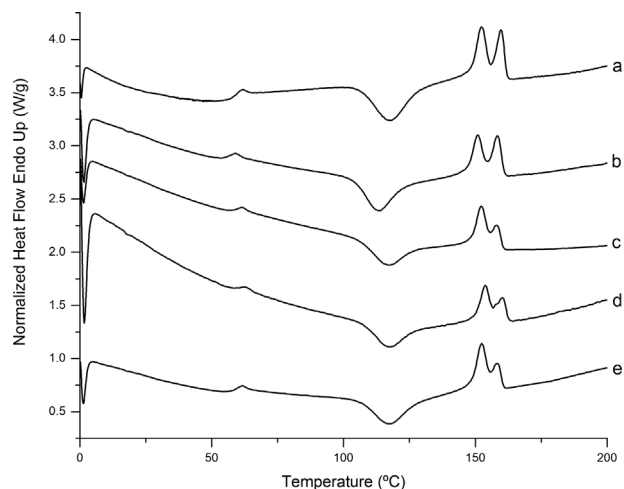


Figure 6. DSC heating curves of the PLA and PLA/*starch-g*-PEHA blends of various w/w compositions: a) 100/0, b) 90/10, c) 80/20, d) 70/30, e) 60/40 (2nd heating scans, heating rate = $10^\circ\text{C min}^{-1}$).

Despite some reports that starch particles can act as nucleating agents to enhance crystallization in PLA,^[33–35] the results in Table 2 offer no supporting evidence for this. Following cooling from the melt at $10^\circ\text{C min}^{-1}$, the second scan's initial (X_i) and final (X_f) % crystallinities are all within the 2–4 and 27–35% ranges respectively with no obvious trend. This indicates that the starch-*g*-PEHA content did not have a significant effect on the PLA's crystallizability either during cooling from the melt or reheating in the solid state. The appearance of twin melting peaks, as seen in Fig. 6, is generally attributed to the formation of two distinct crystallite size populations as a consequence of the melting-cooling-remelting cycle. However, in the case of PLA, it has been reported that the twin melting peaks appear to be related to the melting of the α' (disordered) and α (ordered) crystalline phases, the relative amounts of which depend on the sample's previous thermal history.^[36] This conclusion was supported by the observation that, under suitable high-temperature annealing conditions, the two melting peaks tended to merge into one as a result of the α' - α phase transition.

With regard to thermal stability, the TGA curves of all of the PLA/*starch-g*-PEHA blends showed similar thermal decomposition (initial weight loss) temperatures in excess of 250°C . The TGA curve of the PLA/*starch-g*-PEHA 60:40 blend is shown in Figure 7 as an example alongside those of the separate PLA, starch, and PEHA components for comparison. The curves show that blending with the starch-*g*-PEHA did not lower the thermal stability of the PLA which is important from a melt processing point of view. Even though melt blending was not part of this study, these results indicate that the PLA/*starch-g*-PEHA blends could be safely melt blended and processed within the temperature range (190 – 210°C) normally used for PLA without significant thermal degradation.

3.2.2. Light Transmittance

The percent light transmittance (%*T*) values of the solution-cast films are compared in Table 2. They were measured at a wavelength of 500 nm with air as the reference on $2 \times 2 \text{ cm}$ square samples of thickness $0.065 \pm 0.005 \text{ mm}$. The %*T* values were calculated from the equation:

$$\%T = I_s/I_o \times 100\% \quad (6)$$

where I_s = transmitted light intensity with a sample in the beam, I_o = transmitted light intensity with no sample in the beam.

As a rough guide, samples with %*T* values of <30%, 31–45%, 46–75%, and >75% are generally classified as being opaque, semi-translucent, translucent, and transparent respectively. On this basis, the %*T* values in Table 2 indicate that, while the PLA film alone was transparent, the PLA/*starch-g*-PEHA 90/10 film was semi-translucent, and the 80/20, 70/30, and 60/40 films were all opaque. While the loss of optical clarity with starch content was to be expected due to the light scattering of the starch particles, it was noticeable that this loss occurred particularly sharply above the 10% level. This suggests that the sharp decrease in %*T* may have been due not only to the increase in the starch concentration but also to the partial aggregation of the starch particles. An increase in the size of

Table 2. Summary of the various properties of the PLA/starch-g-PEHA blended films for different blend compositions.

Property	PLA/starch-g-PEHA blended films (w/w)				
	100/0	90/10	80/20	70/30	60/40
Temperature transitions					
Glass transition temperature, T_g ($^{\circ}\text{C}$) ^{a)}	58	56	59	60	59
Crystallization temperature, T_c ($^{\circ}\text{C}$) ^{b)}	118	113	117	117	118
Melting temperatures, T_m ($^{\circ}\text{C}$) ^{c)}	152, 156	151, 155	152, 155	154, 157	152, 155
Morphology					
Heat of crystallization, ΔH_c (J g^{-1})	26.8	22.7	18.4	17.1	18.7
Heat of melting, ΔH_m (J g^{-1})	30.1	25.3	20.0	18.4	19.8
Initial crystallinity, X_i (%)	4	3	2	2	2
Final (pre-melt) crystallinity, X_f (%)	32	30	27	28	35
Optical and surface properties					
Light transmittance, T (%) ^{d)}	76.5 ± 1.2	41.3 ± 1.1	15.1 ± 1.4	10.1 ± 0.9	4.0 ± 1.3
Water contact angle, θ ($^{\circ}$)	84.6 ± 1.8	88.3 ± 1.6	85.4 ± 1.2	83.2 ± 1.7	86.5 ± 1.4
Tensile properties					
Tensile strength (MPa) ^{e)}	33.4 ± 0.5	17.6 ± 0.4	16.9 ± 0.6	14.6 ± 0.2	12.2 ± 0.3
Elongation at break (%)	2.2 ± 0.2	72.3 ± 6.9	4.3 ± 1.3	1.8 ± 0.4	1.6 ± 0.2
Toughness ($\times 10^3$, J mm^{-3}) ^{f)}	40 ± 2	845 ± 74	58 ± 4	18 ± 2	12 ± 2

^{a)}Taken as the mid-point of the glass transition from the DSC curve; ^{b)}Taken as the crystallization peak minimum from the DSC curve; ^{c)}Taken as the twin melting peak maxima from the DSC curve; ^{d)}Measured at a wavelength of 500nm with air as the reference; ^{e)}Taken as the maximum stress from the stress-elongation curve; ^{f)}Calculated from the area under the stress-elongation curve using Origin data analysis software.

starch aggregates with volume fraction in polymer-starch blends has previously been reported.^[37]

3.2.3. Water Contact Angle

The water contact angle (θ) is a measure of the hydrophilicity, or hydrophobicity as the case may be, of a surface. As the

samples in this work were thin films, the main point of interest was whether some of the grafted starch particles could be distributed at the film surface in sufficient concentration to significantly affect the PLA contact angle. However, as the results in Table 2 show, there is no clear trend in the contact angle values as the starch-g-PEHA content increases while the

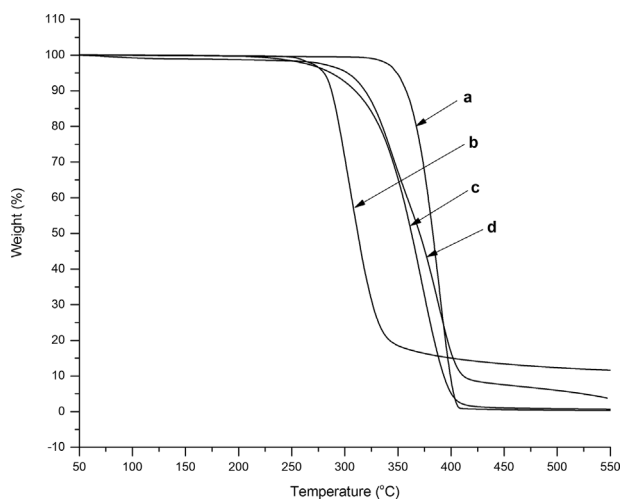


Figure 7. TGA curves of a) PLA, b) starch, c) PEHA, and d) PLA/starch-g-PEHA 60/40 blend (heating rate = $20^{\circ}\text{C min}^{-1}$, N_2 atmosphere).

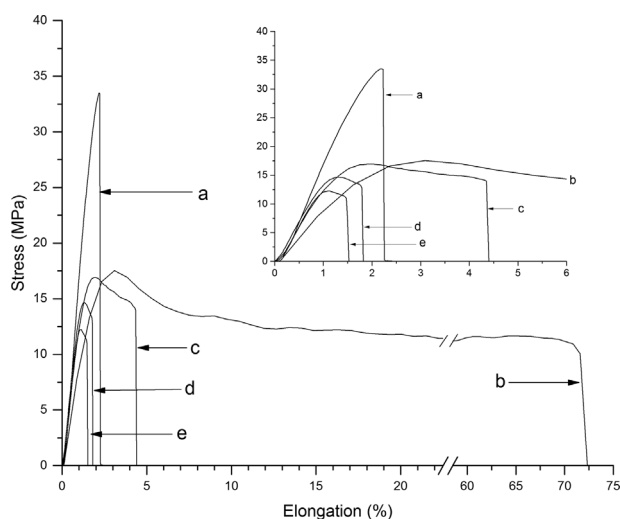


Figure 8. Stress-elongation curves of the PLA and PLA/starch-g-PEHA films of various w/w compositions: a) 100/0, b) 90/10, c) 80/20, d) 70/30, e) 60/40 (gauge length 100 mm, crosshead speed 50 mm min^{-1}).

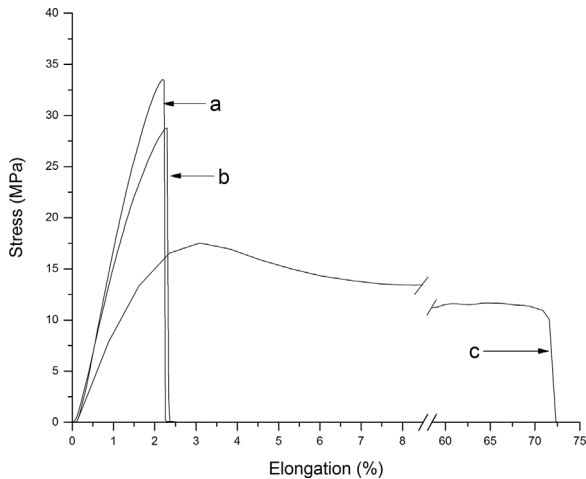


Figure 9. Stress-elongation curves of the a) PLA, b) PLA/starch 90/10 and c) PLA/starch-g-PEHA 90/10 films (gauge length 100 mm, crosshead speed 50 mm min^{-1}).

differences from that of the PLA film alone are less than 4° . This suggests that the starch-g-PEHA particles were mainly embedded in the interior of the film matrix, even at their highest concentration in the 60/40 blend. Another plausible explanation is that most of the hydrophobic g-PEHA was probably concentrated at the surface of the starch particles, thereby masking their hydrophilicity.

3.2.4. Tensile Properties

The stress-elongation curves and derived parameters for the PLA film alone and the series of PLA/starch-g-PEHA blended films are compared in **Figure 8** and Table 2. The curves shown are those which were considered to be the most representative for each sample from tests carried out on at least five rectangular-shaped ($12 \text{ cm} \times 1 \text{ cm}$) specimens of thickness $0.065 \pm 0.005 \text{ mm}$ taken from at least three different films. Relative to the PLA film which was typically strong but brittle, by far the biggest improvement in terms of elongation and toughness was shown by the 90/10 film (curve b in **Figure 8**). This can be attributed to the g-PEHA improving the interfacial adhesion between the starch particles and the PLA matrix. However, these improvements came at the expense of tensile strength which showed a 50% decrease. The 80/20 film also showed signs of improvement, although much less than 90/10, while the 70/30 and 60/40 films were weaker and more brittle than the PLA film alone.

These results indicate that, despite the marked improvement at the 10% level, as soon as the starch-g-PEHA content is increased above 10%, the properties start to deteriorate rapidly as starch particle aggregation increases. This observation is consistent with previous reports on PLA/starch blends which also concluded that the starch concentration at which useful materials can be prepared is limited to around 10%.^[11,12] Thus, it appears that, even when chemical modification of the starch improves its interfacial adhesion with the PLA matrix, it does little to hinder particle aggregation.

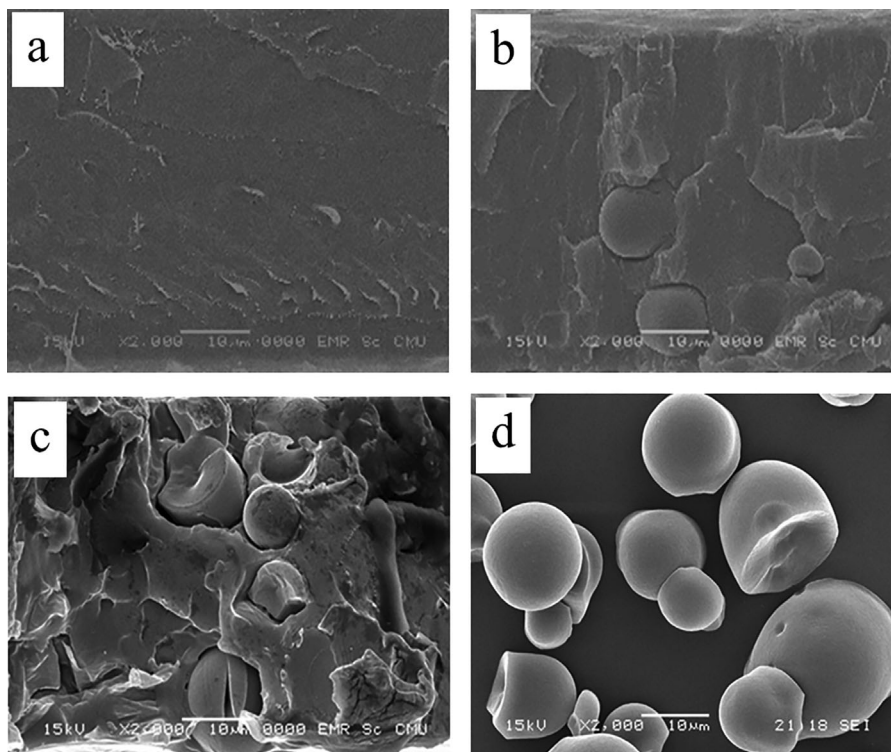


Figure 10. SEM images of the tensile fracture surfaces of the a) PLA, b) PLA/starch 90/10, and c) PLA/starch-g-PEHA 90/10 films and d) the native cassava starch (average particle size = $13.6 \mu\text{m}$) used in this study (magnification $\times 2000$).

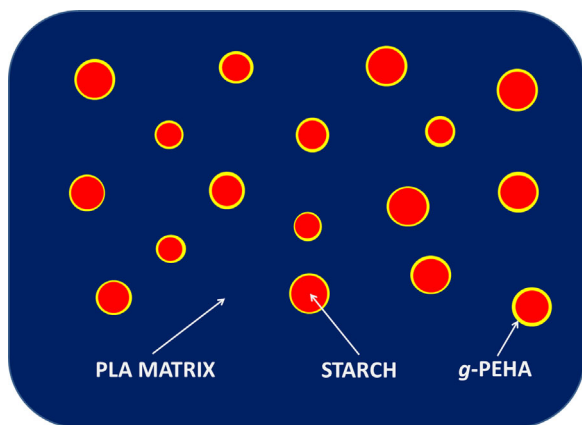


Figure 11. Visualization of the PLA/starch-g-PEHA matrix showing the g-PEHA concentrated at the PLA/starch interface.

Finally, the effect of the g-PEHA modification of the starch is seen most clearly in **Figure 9** by comparison with that of the unmodified starch at the same 10% weight content. Whereas the PLA/starch-g-PEHA 90/10 film shows a marked improvement in elongation and toughness relative to PLA alone, the PLA/starch 90/10 film shows no improvement at all. Indeed, the only effect that the unmodified starch has is to decrease the tensile strength (stress at break) of the PLA, an effect which increases rapidly with increasing starch content. The stress-elongation curves in **Figure 9** can be viewed alongside the SEM images in **Figure 10** of the tensile fracture surfaces of the same test specimens. Whereas the PLA and PLA/starch 90/10 films both show relatively smooth surfaces typical of brittle fracture, the rough PLA/starch-g-PEHA 90/10 surface indicates a ductile fracture consistent with the sample's extensive deformation. Ductile fracture is further supporting evidence of improved interfacial adhesion.

4. Conclusions

These results demonstrate that, despite its various shortcomings as a blend component for PLA, native starch can be chemically modified in order to improve its performance. This chemical modification is aimed primarily at improving the otherwise poor interfacial adhesion (interaction) between the hydrophobic PLA matrix and the hydrophilic starch particles which can result in de-bonding of the two phases, void formation and premature brittle failure. By improving the interfacial adhesion, the modified starch particles can start to contribute toward energy dissipation mechanisms in the PLA matrix under an applied stress which ultimately leads to increased toughness.

In this work, 2-ethylhexyl acrylate (EHA) was chosen as the grafting monomer as it is readily available, relatively inexpensive and its polymer, PEHA, is a soft, tacky material. With this in mind, it was considered that the adhesive properties of PEHA at the macroscopic level could be utilized at the microscopic level to have an interfacial adhesive effect in a PLA/starch-g-PEHA blend. Assuming that most of the hydrophobic g-PEHA is concentrated at the outer surface of the starch particles, its presence at the interface between the starch particles and the

PLA matrix has a compatibilizing effect which helps to lessen the tendency for interfacial separation. A simplified representation of what the blend matrix might look like is visualized in **Figure 11**.

The results here have shown that, even though an improvement in tensile properties has been achieved, it has only been achieved up to a 10% starch-g-PEHA content. At this 10% level, the reduction in the unit cost of PLA, as mentioned in the 'Introduction', may be minimal once the cost of grafting is taken into account. Therefore, efforts still need to be made to increase this limit by increasing the % grafting but this requires a more detailed study of the grafting conditions used and the choice of redox initiating system. Being able to increase the grafted starch content would also increase the rate of biodegradation although this effect would be offset to some extent by the increased amount of hydrophobic grafted g-PEHA.

In conclusion, the results show considerable potential for the use of starch-g-PEHA as a blend component for PLA in biodegradable plastic packaging. This potential has economic implications for the cassava starch industry. By modifying the properties of native cassava starch through graft copolymerization, its range of application and hence its commercial value can be increased through its use in blending with other polymers.

Abbreviations

CS, cassava starch; EHA, 2-ethylhexyl acrylate; MDI, methylene diphenyl diisocyanate, PHEA, poly(2-ethylhexyl acrylate); PLA, poly(lactic acid); TPS, thermoplastic starch.

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Conflict of Interest

The authors declare that there is no conflict of interest.

Keywords

2-ethylhexyl acrylate, cassava starch, chemically-modified starch, poly(2-ethylhexyl acrylate), poly(lactic acid)

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