Research Article

Thermal Behavior of *Tacca leontopetaloides* Starch-Based Biopolymer

Nurul Shuhada Mohd Makhtar, Miradatul Najwa Muhd Rodhi, Mohibah Musa, and Ku Halim Ku Hamid

Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia

Correspondence should be addressed to Nurul Shuhada Mohd Makhtar; nurul2229@yahoo.com

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Starch is used whenever there is a need for natural elastic properties combined with low cost of production. However, the hydrophilic properties in structural starch will decrease the thermal performance of formulated starch polymer. Therefore, the effect of glycerol, palm olein, and crude palm oil (CPO), as plasticizers, on the thermal behavior of *Tacca leontopetaloides* starch incorporated with natural rubber in biopolymer production was investigated in this paper. Four different formulations were performed and represented by TPE1, TPE2, TPE3, and TPE4. The compositions were produced by using two-roll mill compounding. The sheets obtained were cut into small sizes prior to thermal testing. The addition of glycerol shows higher enthalpy of diffusion in which made the material easily can be degraded, leaving to an amount of 6.6% of residue. Blending of CPO with starch (TPE3) had a higher thermal resistance towards high temperature up to 310°C and the thermal behavior of TPE2 only gave a moderate performance compared with other TPEs.

1. Introduction

Biobased polymer is a polymer derived from natural sources in addition of some additives and accelerator. It can be degraded at certain time and temperature. The intention of using Biobased polymer began since 1980s. The increasing plastic wastes on landfill make researchers conscious to come out with the biodegradable polymer [1]. Biodegradable polymer is referred to the polymers in which it can be fed by microorganism exits such as fungi, bacteria, and algae naturally. Normally these materials undergo biological degradation process and produce CO₂ gas, water, inorganic compounds, and biomass at the end of process. Adversely, synthetic polymer is derived from petroleum based such as polyethylene (PE). Plastic, an example of synthetic polymer, can be categorized into two types which are thermoplastic and thermosetting plastics.

During the last few years, polymers with elastic and rubbery properties known as thermoplastic elastomer have been introduced [2]. Thermoplastic elastomers show both advantages typical of rubbery materials and plastic materials which have characteristics similar to those of rubber that has been vulcanized at a fixed temperature but can also be shaped by common injection molding via the application of heat, just like any other ordinary thermoplastic [3]. These materials are biphasic materials that possess the combined properties of glassy or semicrystalline thermoplastics and soft elastomers and enable rubbery materials to be processed as thermoplastics [4].

The increasing demand of thermoplastic elastomer in the world especially in the automobile industry leads to bring in the Biobased polymer which is expected to have a potential to replace and directly reduce the cost obtaining a thermoplastic elastomer. Therefore, starch which is known as a natural polymer consists of linear polysaccharides (amylose) and branched molecules (amylopectin) that have the capability to promote the elastic properties needed in the development of thermoplastic elastomer [5]. The hydrophilic properties of starch can be modified by blending with synthetic polymer in which have partial environmental degradability to the blends.
Otherwise, the addition of additives or fillers such as glycerol, silica, and carbon black [6] can also enhance the performance of the starch blends.

Carvalho et al. [7] had prepared indirectly a blend of thermoplastic starch and latex of Hevea Brasiliensis. It shows that the addition of small amounts of rubber to the starch blends containing 20% of glycerol had induced their softening properties. A homogeneous dispersion of rubber in the thermoplastic starch matrix was obtained in the presence of the aqueous medium, with rubber particles ranging in size from 2 to 8 mm. Moreover, the presence of nonrubber constituents of latex was responsible not only for insuring the latex stability but also for improving the compatibility between the thermoplastic starch and the natural rubber phases. However, the addition of rubber was limited by phase separation, the appearance of which depended on the glycerol content. It was proven that glycerol contributes to both the plasticization of starch and to the improvement of the starch-rubber interface.

Many papers had been published using common starch such as corn, potato, and wheat as a raw material of biopolymer development. However, these starches have an important role in the human food hierarchy system. Therefore, Tacca leontopetaloides starch, in which the percentage of amylose and amyllopectin is quite similar to corn starch, is able to provide elastic properties and become an alternative to common starch. Moreover, it is not a staple food in Malaysian population. Tacca leontopetaloides also known as Polynesian arrowroot starch is a wild perennial herb belonging to the family Dioscoreaceae. This plant is naturally distributed from western Africa through southern Asia to northern Australia [8–10]. Tacca starch that consists of 22.5% amylose and 77.5% of amyllopectin [11, 12] served as an important food source for many Pacific Island cultures and additionally used to stiffen fabrics in some of the islands [13]. This starch is a perennial herb with a tuberous rhizome, from which a single petiole, 60–90 cm long, arises, bearing deeply lobed leaf blades consisting of three main segments, each further divided in a pinnate manner, and the blades are about 30 cm across [12]. Some of these countries used Tacca as a medicine to treat stomach ailments and also diarrhea and dysentery. However, there is no previous study reporting in using Tacca leontopetaloides starch as a substitute of biopolymer production.

In evaluating the potential of this natural polymer incorporated with additives, the thermal performance analyses of the blends need to be done. Normally, the thermal behavior of materials has been evaluated by using thermogravimetric analysis (TGA), differential scanning chromatography (DSC), DMTA, and NMR. Thermal analysis is probably the oldest chemical testing known and was used by the alchemists in their original primitive chemical explorations [14]. The term thermal analysis is applied to any technique which involves a measurement of a material’s specific property while the temperature is controlled (either changed or maintained) and monitored [15].

The analysis of biopolymer on its thermal characteristics is very important to indicate the suitability of the product to be applied. Various approaches have been adopted to improve the thermal performance of thermoplastic elastomers according to their needed application. On top of that, this research will reveal the thermal behavior of the polymer derived from Tacca leontopetaloides starch with natural rubber and three different plasticizers which are glycerol, palm olein, and crude palm oil. Thermal properties of formulated Biobased polymer will be investigated by using thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC).

2. Materials and Methods

The roots of Tacca leontopetaloides were obtained from the east coast of Peninsular Malaysia. Each plant can produce at least three roots (legumes) with a weight of not less than 500 grams each. Glycerol was purchased from Merck Sdn. Bhd. The natural rubber was provided by the Malaysian Rubber Board (MRB), and rice husk was obtained from BERNAS Rice Mill, Tanjung Karang Malaysia. The roots of Tacca leontopetaloides were grinded, sieved, and soaked in water. The pellet which settled down at the bottom of the container was dried to a constant weight in the oven at 80°C. After drying, the pellet was grinded and sieved to different particle sizes of starch [13].

2.1. Extraction of Silica from Rice Husk. The method of the preparation of silica from rice husk was referred to by Chuaajuljit et al. [16]. Rice husk was thoroughly cleaned with tap water and was mixed with 0.4 M HCl in the ratio of 100 g husk per 1-liter acid. Then, it was heated until boiled before the mixture temperature was maintained at 105°C for 3 hours. The acid was completely removed from the husk by washing with tap water. It was then dried overnight in an oven at 110°C. The treated husk was calcined in an electric furnace at 600°C for 12 hours. Silica was obtained in the form of white ash wherein the shape of the silica is similar to the shape of the husk. Therefore, the silica was grinded into powder prior to blending with starch and rubber.

2.2. Preparation of Starch TPEs. Starch was added in boiled water and vigorously mechanically stirred at 95°C until the suspension became transparent. The starch suspension was then blended with glycerol until it became a homogeneous mixture. Later, latex natural rubber with sieved silica from rice husk was added and mixed manually until a homogeneous mixture was obtained. TPEs were prepared with respect to per hundred rubber (phr) as used in Table 1. Then calcium chloride, CaCl₂, solutions were used to coagulate the mixture. The coagula was thoroughly washed with water and dried at 80°C until the moisture content was less than 2%. The dried compound was mixed with stearic acid, which acts as a softener, and curing agent, and sulfur, by using two-roll mill, followed by vulcanization process at 70°C [17]. The same method was used for palm olein and crude palm oil plasticizer.

2.3. Fourier Transform Infrared (FT-IR) Analysis. Fourier transform infrared (FT-IR) spectra were recorded on a Perkin Elmer FT-IR spectroscopy. Samples were analyzed by
scanning the wavelength between 4000 and 515 cm\(^{-1}\). The infrared spectroscopy detects the vibration characteristics of chemical functional groups in the sample.

2.4. Differential Scanning Calorimeter (DSC) Analysis. The samples were coated with aluminum pans. All measurements are made under a nitrogen gas atmosphere at a heating rate of 10 °C min\(^{-1}\) and samples weighing about 6 mg. The thermal properties during the melting process of each sample were investigated. Temperature in which the material started to melt is defined as \(T_m\) (melting temperature), and the heat required to change the state of material is defined as \(\Delta H_m\), (heat change of melting).

2.5. Thermogravimetric Analysis (TGA). The thermal stability of samples was investigated by using thermogravimetric analysis TGA (METLER TOLEDO TGA SDTA851). Samples were weighed and heated starting from room temperature to 500 °C using a heating rate of 10 °C min\(^{-1}\) in an ambient air environment. The decomposition of thermoplastic was recorded.

3. Results and Discussion

3.1. Fourier Transform Infrared (FTIR) Analysis. The infrared (IR) spectra of Tacca leontopetaloides starch/natural rubber blends incorporated with glycerol, palm olein, and crude palm oil and without plasticizer were labelled as TPE1, TPE2, TPE3, and TPE4, respectively, in Figure 1. Meanwhile, Table 2 shows the scanning absorption peaks of samples and their functional group. It shows that the spectrum wave of pure starch (Figure 1) exhibited a strong absorption peak at 1015.84 cm\(^{-1}\) which indicates the presence of ether compounds with molecular motion of carbon to carbon oxygen stretching vibration. It validates that this starch consists of amylose and amylopectin which has been built up by a long chain of monosaccharide, a simple sugar from a new starch between 4000 and 515 cm\(^{-1}\) that acts as a hydrophilic character and ether (C–O–C) which is represented by cellulose [18].

The addition of glycerol (TPE1) in the blending contributed to the formation of a strong hydrogen bond of the hydroxyl group that exists in the structure of starch.

Therefore, the absorption peaks at 3352.81 cm\(^{-1}\) in pure starch spectrum reduced to 3325.18 cm\(^{-1}\) which indicates the increasing of strength in the hydrogen bonding between glycerol and the structure of starch [19]. In addition a new peak was observed at 2850.70 cm\(^{-1}\) showing that the molecular weight of TPE1 was increasing as the bond between carbon and hydrogen was bending (C–H) with increasing of starch. Furthermore, glycerol also contributed to the increasing of C=O vibration in starch, as the absorption peak increased at 1646.91 cm\(^{-1}\) in pure starch to 1662.06 cm\(^{-1}\).

Instead, the addition of olein oil (TPE2) and crude palm oil (TPE3) caused the absorption peak to decrease from 3352.81 cm\(^{-1}\) (pure starch) to 3348.60 cm\(^{-1}\) and 3350.47 cm\(^{-1}\), respectively. However, new absorption peaks were obtained at 1746.38 cm\(^{-1}\) (TPE2) and 1745.62 cm\(^{-1}\) (TPE3) which represent the vibration of carbon double bond to oxygen in aldehyde. It validates that the presence of C=O in structural starch consequently caused the increase of molecular weight of samples and reduced the strength between plasticizer and structural starch.

As expected, without a plasticizer, the bends in pure starch undergo a minor shift from 3352.81 cm\(^{-1}\) to 3352.40 cm\(^{-1}\) (TPE4) but still had an increment in the hydrogen bonding between water and starch. On the other hand, the absorption peaks between 1375 and 1448 cm\(^{-1}\) represent N=O bending of methane that appeared because of the addition of latex natural rubber in starch which contained ammonia.

3.2. Differential Scanning Calorimetry (DSC) Analysis. Differential scanning calorimetry (DSC) analysis method has been used to study the heat transfer during physical and chemical processes. It measures the exothermic and endothermic transitions as a function of temperature. In this analysis, when a melting process occurs, the samples will absorb energy (endothermic process). The characteristic of melting process presence is shown in Figure 2. Generally, three endothermic peaks were observed for all TPEs, in which the first range was between 100 and 200 °C (evaporation of moisture), the second range was between 200 and 300 °C (plasticizer), and the final one was between 400 and 500 °C (natural rubber). It can be seen in Table 3 that the heat change of melting process for TPE3 was three times lower than other TPEs for all regions. The melting temperature for TPE3 was slightly decreased from 136.35 °C (TPE4) to 106.87 °C. Meanwhile, the melting temperature, \(T_m\), of TPE4 decreased from 136.35 °C to 61.94 °C (TPE2) when palm olein was added into starch. Moreover, the addition of glycerol in TPE1 had made this material to absorb higher heat and change the phase to a value from

<table>
<thead>
<tr>
<th>Composition [phr]</th>
<th>Natural rubber</th>
<th>Starch</th>
<th>Glycerol</th>
<th>Palm olein</th>
<th>Crude palm oil</th>
<th>Rice husk silica</th>
<th>CaCl₂</th>
<th>Sulphur</th>
<th>Stearic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPE1</td>
<td>100</td>
<td>12.5</td>
<td>20</td>
<td>—</td>
<td>—</td>
<td>1.25</td>
<td>1.25</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>TPE2</td>
<td>100</td>
<td>25</td>
<td>—</td>
<td>22.5</td>
<td>—</td>
<td>2.5</td>
<td>2.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>TPE3</td>
<td>100</td>
<td>25</td>
<td>—</td>
<td>22.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>TPE4</td>
<td>100</td>
<td>25</td>
<td>—</td>
<td>—</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

\(^{1}\)Ratio of Tacca leontopetaloides starch to H\(_2\)O was 1:10.
Table 2: Summaries of functional group in pure starch and starch incorporated with glycerol (TPE1), olein oil (TPE2), and crude palm oil (TPE3) and without plasticizer (TPE4).

<table>
<thead>
<tr>
<th>Types of vibration/samples</th>
<th>Pure starch</th>
<th>TPE1</th>
<th>TPE2</th>
<th>TPE3</th>
<th>TPE4</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H stretch in carboxylic acid</td>
<td>3352.81</td>
<td>3325.18</td>
<td>3348.60</td>
<td>3350.47</td>
<td>3352.40</td>
</tr>
<tr>
<td>C=O stretching to CH₃ in aldehydes group</td>
<td>—</td>
<td>—</td>
<td>1746.38</td>
<td>1746.38</td>
<td>1733.81</td>
</tr>
<tr>
<td>C=O stretch to amides</td>
<td>1646.91</td>
<td>1662.06</td>
<td>1661.82</td>
<td>1651.56</td>
<td>1661.75</td>
</tr>
<tr>
<td>N=O bend to C–H₂</td>
<td>—</td>
<td>1435.37 and 1375.30</td>
<td>1447.98 and 1375.57</td>
<td>1448.20 and 1375.55</td>
<td>1446.81 and 1375.42</td>
</tr>
<tr>
<td>C–O stretching to an ether</td>
<td>1015.84</td>
<td>1027.84</td>
<td>1037.64</td>
<td>1016.43</td>
<td>1015.4</td>
</tr>
</tbody>
</table>

48.55 J/g and 116.88 J/g, compared to other TPEs. Based on this, the addition of glycerol shows a higher decomposition rate which will be further discussed in the thermogravimetric analysis. TPE4 (without plasticizer) shows higher heat change (153.63 J/g) at first region which represents the evaporation of moisture since TPE4 was only incorporated with water. Therefore, it consists of high moisture content compared with other TPEs. It can be concluded that the oil-based plasticizer could cause lower melting temperature for evaporation of moisture content in formulated TPEs.

3.3. Thermogravimetric Analysis (TGA). A comparison of the weight reduction of TPE1, TPE2, TPE3, and TPE4 towards thermal degradation was done by using TGA at a heating rate of 10° C min⁻¹, wherein the samples were being heated starting from room temperature to 500°C (Figure 3). The thermogravimetric analysis (TG) is shown in Figure 3(a), and derivative thermogravimetric analysis (DTG) is shown in Figure 3(b). Thermograms obtained for TPEs were compared with the thermograms of pure starch and natural rubber (NR). The results obtained show that a rapid drop in the
Table 3: Properties of melting process undergone at 100–200 °C, 200–300 °C, and 400–500 °C.

<table>
<thead>
<tr>
<th>Samples/peaks’ region</th>
<th>100–200 °C</th>
<th>200–300 °C</th>
<th>400–500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( T_m ) (°C)</td>
<td>( \Delta H_m ) (J/g)</td>
<td>( T_m ) (°C)</td>
</tr>
<tr>
<td>TPE1</td>
<td>146.64</td>
<td>146.64</td>
<td>242.96</td>
</tr>
<tr>
<td>TPE2</td>
<td>61.94</td>
<td>110.37</td>
<td>226.24</td>
</tr>
<tr>
<td>TPE3</td>
<td>106.87</td>
<td>34.75</td>
<td>244.51</td>
</tr>
<tr>
<td>TPE4</td>
<td>136.35</td>
<td>153.63</td>
<td>244.63</td>
</tr>
</tbody>
</table>

The maximum decomposition rates of TPEs were analyzed by using DTG thermograms (Figure 3(b)). It was revealed that three steps were involved in the thermal degradation of the TPE1 and two steps were showed for the TPE2, TPE3, and TPE4. Two peaks were found in the thermal degradation of TPEs where maximum decomposition temperature was attained for starch and NR. The maximum temperature, \( T_{max} \), decomposition for pure starch and NR was 302.84 °C and 371.32 °C (Figure 3(b)), respectively. However, the thermogram of TPE2 shows that the first peak between 50 and 100 °C could be the peak of moisture evaporated from TPE2. Commonly, the first stage from 0 to 160 °C is allocated to water evaporation [20].

The DTG thermogram of TPE1 had revealed a peak at a maximum temperature of 188.99 °C in which it represents the evaporation of glycerol. As stated by Gómez Siuriana et al. [21], the peak exhibited at a range between 110 °C and 220 °C indicates the loss of volatile components and nonpolymeric constituents of the sample such as glycerol. The decomposition of starch for each TPE formulated was revealed at temperature range between 230.31 °C and 287.62 °C. Starch is known to be composed by amyllose and amyllopectin. The temperature range between 280 °C and 380 °C relates with the different decomposition rates of amyllose and amyllopectin chains and the network structure of the cellulose, wherein amyllose chains were decomposed first due to their linear structure [22]. Another main material in TPE was natural rubber (NR) in which the decomposition of NR in TPEs was found between 337 °C and 444 °C. The DTG (Figure 3(b)) of TPEs also shows that a higher temperature was needed to decompose TPEs with plasticizer (350 to 400 °C) compared with the decomposition temperature of pure starch (300 °C) which was much lower. This supports the FTIR result in Figure 1 where the absorption peak of TPEs spectrum seems to be increased, which indicates the increment amount of carbon atom. As already known, when carbon increases it will directly increase the intermolecular forces; thus, more temperature is needed to break the bond.

The rate of weight reduction for starch in TPE4, which was 0.73 mg min⁻¹, was higher compared to TPE1 and TPE3 with a value of 0.33 mg min⁻¹ and 0.53 mg min⁻¹, respectively, while the rate of weight reduction of NR for TPE3 was 1.97 mg min⁻¹ which was higher compared to TPE1, TPE2, and TPE4 with a value of 1.74 mg min⁻¹, 1.53 mg min⁻¹, and 1.94 mg min⁻¹, respectively. Based on the results, it is validated that the modification of starch by using glycerol, palm olein, and crude palm oil, as well as the interaction between starch and NR does affect the rate of weight reduction. It
seems that the rate of weight reduction for starch and NR was reduced in TPEs compared to the rate of weight reduction for pure starch and NR alone.

4. Conclusion

The thermal behavior of *Tacca leontopetaloides* starch/natural rubber blends was investigated. The addition of glycerol in the blending had increased the hydrogen bonding between starch and glycerol and required more heat to undergo the diffusion process. This resulted in the plasticized starch to easily decompose and leave about 6.6% residue as analyzed by TGA. Olein oil incorporated with starch gives moderate performance on the thermal behavior compared to the addition of crude palm oil which shows higher thermal resistant. Hence, it can be concluded that glycerol can be used to incorporate with *Tacca* starch in order to develop green polymer that will promote the degradability properties while it is no longer in use. Meanwhile, in the application requiring high thermal resistant such as automobile industries, crude palm oil incorporated with *Tacca* starch is the most suitable plasticizer that can be used.

Conflict of Interests

The authors hereby declare that the following organizations: Research Management University of Technology Mara Shah Alam, Malaysia, Syarikat BERNAS Rice Mill, Tanjung Karang, Malaysian Rubber Board (MRB), and Merck Sdn. Bhd, which directly and/or indirectly contributed to this research paper, have no involvements that might raise the question of bias in the work reported or in the conclusions, implications, or opinions stated, and there is no conflict of interests.

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