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The Effect of Natural Rubber and Plasticizer Addition on the Mechanical Properties of *Tacca leontopetaloides* Starch Based Polymer

Nur Farzana Abdul Ghafar[1,a], Nur Shahidah Ab Aziz[2,b],

Nurul Shuhada Mohd Makhtar[3,c] and Miradatul Najwa Mohd Rodhi[4,d]

[1,2,3,4]Faculty of Chemical Engineering, Universiti Teknologi MARA, Malaysia

[a]nurfarzana_abdghafar@yahoo.com*, [b]shahidah_aziz@salam.uitm.edu.my*,
[c]nurul2229@yahoo.com*, [d]miradatul@salam.uitm.edu.my

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Abstract. The effect of natural rubber and glycerol addition on the mechanical performance of *Tacca leontopetaloides* biopolymer was investigated in this paper. The samples were formulated by varying blend ratios of latex natural rubber to glycerol; 40/30 (GM1), 50/5.85 (GM2), 60/30 (GM3), 40/10 (GM4) and 50/20 (GM5). The samples (GMs) were compounded by using two roll mill machine followed by vulcanization process with the presence of stearic acid and sulphur that act as curing agent. The sheet formed was cut into desired sizes, based on the analysis conducted. The mechanical performance of GMs was investigated by conducting tensile test, morphological structural analysis and water absorption test. The mechanical properties of GM2 showed a high tensile strength with low Young's modulus compared to other GMs, thus indicating that GM2 was the superior combination of natural rubber to glycerol blend ratio. This, therefore, may be applied for the development of biopolymer with the properties of thermoplastic elastomer.

Introduction

Petroleum-based polymers have been widely used for years in industries. These polymers have great ability in terms of mechanical properties. However, as years passes by, the availability of petroleum has been decreasing and the price gets higher. In addition to that, the biochemical inertness of petroleum-based products had proven disastrous for natural polymers market [1]. Since then, due to the environmental issues and petroleum shortage, the level of understanding of the potentiality and ability of biopolymers have attracted an increasing amount of attention from researchers, scientists and material developers in industries. Biopolymers are natural polymers produced from renewable resources such as corn and sugarcane [2]. As natural polymers, they possess high sensitivity of moisture that could lead to premature degradation and also low softening temperature. These limitations are well studied and thus, reinforcement with fillers and plasticizers are one way in overcoming those limitations [3]. In automotive industry, biopolymers are being applied in interior parts of car such as dashboard, door trim, floor mat; and seat cover [4].Starch is the most promising, abundant and cheap biopolymers used in industries to produce thermoplastic starch (TPS). However, TPS presenting several limitations such as low degradation temperatures which leads to processing difficulties, poor mechanical properties and high water susceptibility [5]. In this study, the source of starch was obtained from a rare species of a flowering plant in the yam family called *Tacca leontopetaloides* or generally named as seashore bat lily. By utilizing *Tacca leontopetaloides* starch, the properties improvement of TPS with the addition of natural rubber and glycerol plasticizer are studied in terms of their mechanical properties.

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Methodology

Raw materials

Tacca leontopetaloides starch used in the study was obtained from East Cost of Peninsular Malaysia; latex natural rubber (LNR) was supplied by Malaysian Rubber Board (MRB); rice husk was supplied by Bernas Rice Mill TanjungKarang, Selangor; glycerol was provided by Merck (M) Sdn. Bhd. while calcium chloride, stearic acid and sulphur was obtained from R&M Chemicals.

Silica preparation

The silica used in the study was produced from rice husks (RH) which was collected and thoroughly cleaned with tap water and undergone 24 hours of drying at 110°C in an oven (Memmert LTE 500). Cleaned RH was immersed in 0.4M HCl solution with a ratio of 100g RH to 1L HCl with a heating temperature of 105°C for 3 hours. After heating, the colour of RH has changed to dark brown and it was then rinsed with tap water and dried in the oven for 24 hours. The treated RH was calcined in an electric furnace (Vulcan 3-550) at 600°C for 24 hours in which white ash powder was formed. The rice husk silica (RHS) powder was sieved to a desired size of about 106 µm.

Preparation of green materials

Green materials (GM) may refer to the combination of *Tacca leontopetaloides* starch and LNR which were prepared by melt blending technique using a beaker and a hot plate. An amount of 10 g of *Tacca leontopetaloides* starch was added to a beaker containing 150 ml of distilled water (dH_2O). The solution was consistently heated at a temperature of 150°C. The solution was continuously stirred using a magnetic stirrer at 150 rpm then, 1 g of silica and glycerol were added into the solution. The glycerol used was volume-varied at 5.86%, 10%, 20% and 30%. At ambient temperature, LNR was then added into the blending together with 1 g of calcium chloride to stabilize the composition of the green materials. The natural rubber used was also volume-varied at 40%, 50%, and 60%. Once the blend was well-mixed, it was dried in the oven at 110°C for 24 hours. The dried sample of GM was rolled using two roll mill (ServitexPolymix 110L) at a temperature ranging from 50 to 60°C until it formed a sheet with a thickness of 2.5 mm. During the compounding process, 0.2 g of each sulphur and stearic acid were mixed together with the GM sample. The finished product of GM sample was then cut into desired sizes according to analysis to be performed. The composition of GM samples prepared is shown in Table 1.

Table 1: Compositions of green materials

Sample	LNR (%)	Glycerol (%)	Starch (g)	dH_2O (ml)	RHS (g)	$CaCl_2$ (g)
GM1	40	30	10	150	1	1
GM2	50	5.86	10	150	1	1
GM3	60	30	10	150	1	1
GM4	40	10	10	150	1	1
GM5	50	20	10	150	1	1

Fourier Transform Infrared (FT-IR).

Fourier Transform Infrared Spectrophotometric (FTIR) (Perkin Elmer) was used to analyze the functional group exhibited in the GM samples. It was operated thermally by compressing the samples into a thin film or in form of sheet. The weight of each sample to be analyzed was about ≤5 mg. The GM samples were scanned at resolutions of 400 to 4000 cm^{-1} and 4 cm^{-1}.

Mechanical properties.

Mechanical properties were conducted according to the ASTM D412-06 method by using universal testing machine (Tinius Olsen H50KT) with a load cell of 5 kN at a crosshead speed of 50 mm/min. Five GM samples with a dimension of 100 mm × 25 mm × 2.5 mm±0.5 mm were

prepared. All five samples were tested at 100% and 300% elongation, respectively. Values obtained for the tensile strength, elongation at break and Young's modulus for each sample was reported.

Morphological structural analysis.

The morphologies of all five GM samples were investigated using Field Emission Scanning Electron Microscopy (FESEM) using Zeiss DSM-960 Scanning Electron Microscope. Before the test was conducted, the GM samples were coated with palladium using Bal-Tec SCD005 Sputter Coater. The surface of each sample was analyzed at magnifications of 300X and 1000X. The surface appearances of the samples were observed and the sizes of voids present in the samples were determined.

Water uptake analysis.

Water absorption test was done according to the ASTM D570-98 method. A rectangular sheet of each GM sample with a dimension of 76.2 mm × 25.4 mm × 2.5 mm±0.5 mm was prepared. All five GM samples were left in a beaker containing distilled water for a 24-hour immersion. After 24±½-0 hour, the samples were taken out one at a time and the excess water on the surface of the sample was wiped off with dry cloth. The GM sample was then immediately weighed using Shimadzu TX323L electronic balance.

Results and discussion

Fourier Transform Infrared (FTIR) analysis

The composition of blending samples consist of starch with various volumes of natural rubber and glycerol. Fig. 1 shows the analysis of FTIR spectra for GM samples by indicating the present of functional groups and study the effectives of GM samples after adding natural rubber and glycerol during the compounding process. The absorption peaks were detected at functional group of hydroxyl group, methyl group, C-H stretch, nitro group, ether stretch, and vinyl group, C-C=C asymmetric stretch[6]. The assignment of each functional group can be shown as Table 2.

Table 2: FTIR assignment of green material samples

Wavenumber (cm^{-1})	Functional Group
3400-3450	Hydroxyl group (O-H bond)
2800-3000	Methyl group (C-H stretch)
1450-1600	Nitro group
1400-1500	Vinyl group (C-C=C asymmetric stretch)
1000-1300	Ether stretch

Fig. 1(a) represent the native starch which indicates the stretching vibration of hydroxyl group. After addition of natural rubber and glycerol to the composition of GM, the vibration of samples changes as illustrated in Fig. 1 (b-f). As high amount of natural rubber was added to composition, the hydroxyl group was omitted and caused the h-bond to split from the group and attached to C-H stretch group. The presence of the nitro group makes the sample more stable due to the presence of natural rubber which causes the h-bond to directly increases proportionally with molecular weight and yield more rubbery effect to the sample. The addition of glycerol causes the functional group ester present each GM samples. As high amount of glycerol added to the samples, the molecular weight increases as well as the bonding of ether increases which causes GM samples more unstable.

Mechanical properties

The corresponding data for tensile strength (TS), elongation at break (E) and Young's modulus (M) are tabulated in Table 3 and the stress-strain curves are shown in Fig. 2 and Fig. 3. Both plots show linearity of the stress-strain in which, with the increasing content of natural rubber, the stress of the blends improved while the strain declined. Similar to previous study [7], the stress-

strain curves showed typical pattern of rubbery starch plastic materials, as the plots are essentially linear at low strain and curved towards the strain axis at higher strains. The performance of the samples within the range of 40-50% natural rubber content shows strong hydrogen bonds formed in GM samples with the additional improvement by glycerol. This hydrogen interaction has improved the stress and Young's modulus of the blends. As referred to the tabulated data in Table 3, it shows the mechanical properties of the samples where it displays that the samples were complimented with higher tensile strength and slightly lower elongation at break at 100% elongation compared to 300% elongation. The lower elongation at break shows a requirement of higher applied stress for the composites to rupture, hence increasing the tensile strength [8].

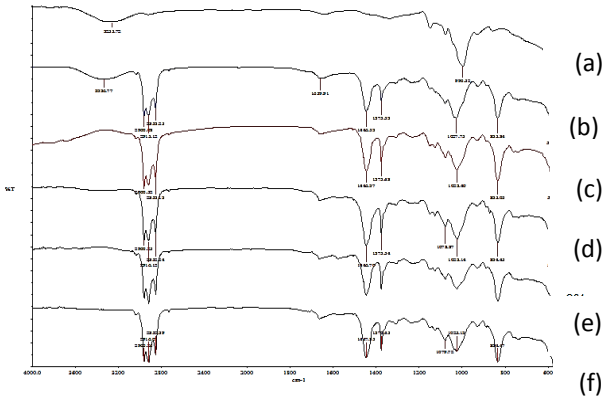

Fig.1: FTIR spectra of the GM samples; (a) Starch, (b) GM1, (c) GM2, (d) GM3, (e) GM4 and (f) GM5.

Table 3: Values of tensile strength (TS), elongation at break (E) and Young's modulus (M) at elongations of 100% and 300%

Sample	TS (MPa)		E (mm)		M (MPa)	
	100%	300%	100%	300%	100%	300%
GM1	1.083	0.939	540	534	0.1488	0.4528
GM2	1.467	2.122	696	822	0.0912	0.4968
GM3	0.933	0.891	516	578	0.1008	0.4528
GM4	1.019	1.136	494.4	580	0.1760	0.5070
GM5	0.720	0.709	726	752	0.0272	0.2288

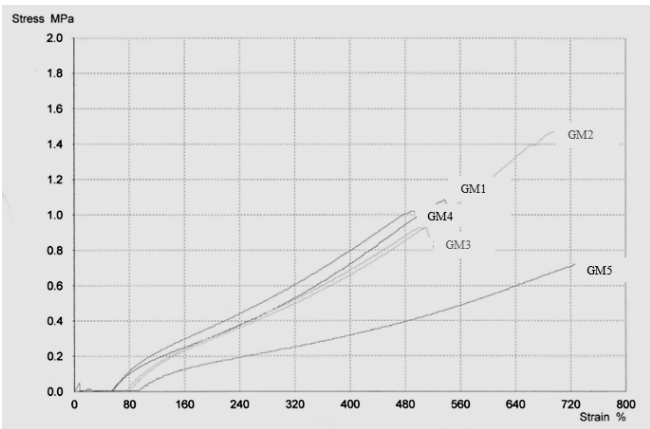

Fig. 2: Stress-strain curves of GM samples at 100% elongation.

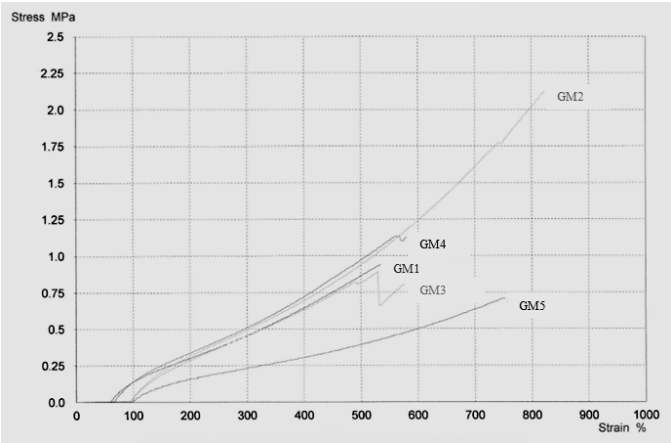

Fig. 3: Stress-strain curves of GM samples at 300% elongation.

Based on both plots, it is obvious that GM2 represents better mechanical performance than the remaining samples. It possesses 50% of rubber content and 5% of glycerol content which shows a high amount of rubber and low amount of plasticizer. It proves the possibility to produce biopolymer with good mechanical properties. Since the mechanical properties of plasticised starch can decrease with the increase in the amount of plasticiser [9], then the presence of natural rubber together with rice husk silica filler compensate the weakness by enhancing the adhesion between the phases [9, 10]. This shows the in-situ compatibilization that makes the mechanical properties of GM samples was improved. Furthermore, a good adhesion between filler and GM sample shows a strong interface which makes it possible to handle high stress with the natural rubber presence as a compatibilizer [11]. This result may be strengthen by the previous analysis where the characterization of the samples by FTIR discovered that the presence of nitro group by the addition of high natural rubber content increases hydrogen bond thus gives the rubbery effect to the sample while the presence of ester group by the addition of low glycerol content makes the sample become a much stable compound.

Morphological structural analysis

Field Emission Scanning Electron Microscopy (FESEM) micrographs of the samples are depicted in Fig. 4. The figure displays the dispersed phase of rubber as particles homogenously distributed in the GM samples. The addition of glycerol seems to contribute in the plasticization of the starch as well as the improvement of the starch-rubber interface [1]. As can be seen in Fig. 4(e), the blending of 50% LNR and 20% glycerol was observed to have resulted in a smooth surface while the other four samples were observed to have similar rough surfaces. The occurrence of rough surfaces may result from the dispersion of natural rubber in the sample of materials, in which the amount of natural rubber in the sample is high. The high content of natural rubber makes it difficult to homogenously distribute in the GM samples and thus leads to unstable dispersed phase contributing to undesirable appearance [12]. Considering the fact that starch and natural rubber were incompatible [5, 13], this shows poor adhesion between the components of the blends. With smooth surface possessed by GM5, it is considerable to have good performance, but the presence of large void becomes a risen factor. Among the five samples, corresponding to the blend of 40% natural rubber and 10% glycerol, GM4 was observed to be quite possible to have a good adhesion. This is because the visible voids in the sample were considered to be the smallest with measured diameters of 2.904 μm and 5.749 μm, as shown in Fig. 4(i). Moreover, as in complimenting the previous section, GM2 that possessed voids with diameters of 0.961 μm and 9.572 μm, has similar potentiality as GM4 offered which can be referred in Fig. 4(g). With comparison between GM2 and GM5, the amount of voids present in the samples is also being considered as it leads to water absorption, which will be discussed later in the next section.

Table 4: Sizes of voids present in GM samples.

Sample	Sizes of voids (μm)
GM1	4.469, 10.130
GM2	0.961, 9.572
GM3	5.510, 28.680
GM4	2.904, 5.749
GM5	0.706, 4.048, 21.67

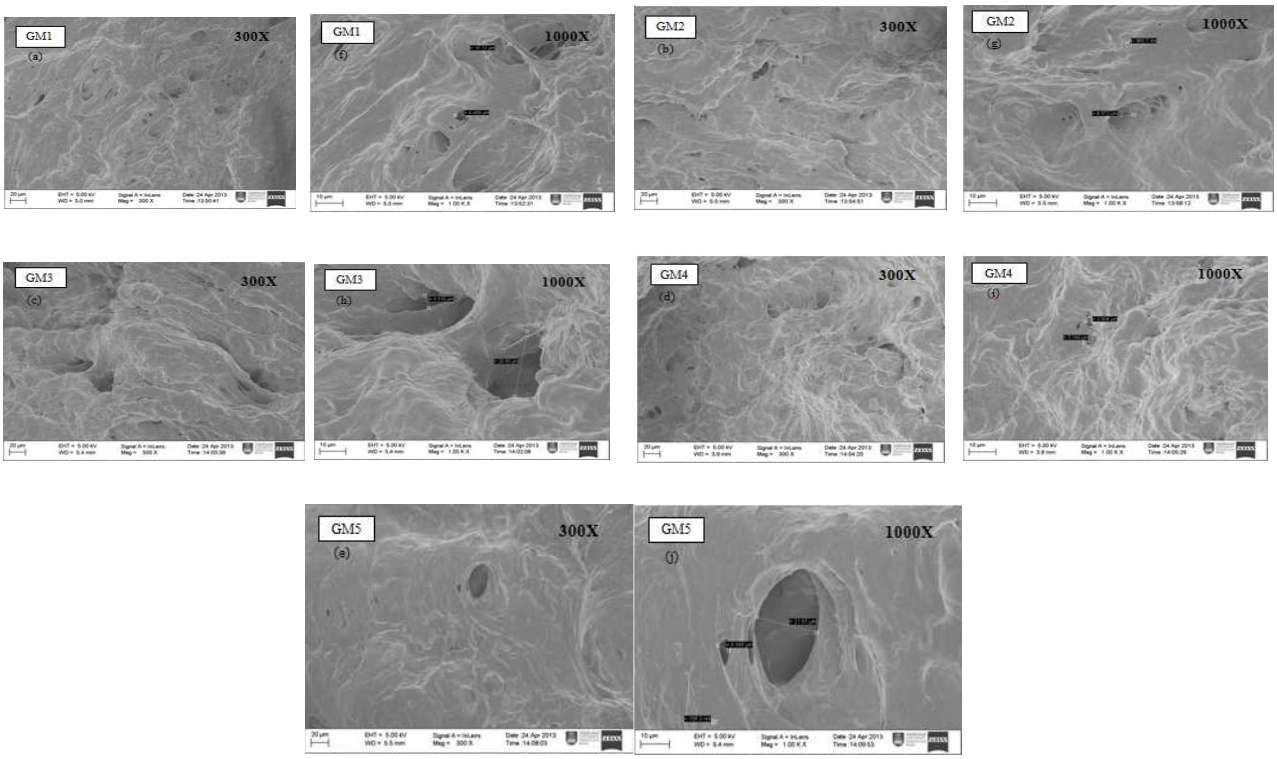

Fig. 4: FESEM micrographs of the GM samples with two different magnifications; 300X and 1000X.

Water uptake analysis

Fig. 5 shows the percentage of water absorbed by the samples after a 24-hour immersion was conducted. It can be seen that GM4, the sample with 40% rubber and 10% glycerol, contributes to the highest amount of water absorbed. The less amount of rubber resulted in high susceptibility to water due to less cross-linked rubber particles [8]. The less cross-linkage contributes to poor adhesion and distribution of components in the sample. It increased void and gap between components and thus increased the penetration of water molecules into the sample. As starch has hydrophilic nature, the percentage of water uptake by the blends of GM may increase. However, the dynamic cross-linking between the filler and TPS matrix made it possible in reducing penetration of water molecules into the samples [14]. This can be proven from Fig. 5 where GM5 that possess higher rubber content, resulted in higher cross-linked rubber particles that makes the blend becomes stiffer and less penetrable by the water molecules, which later results with the least amount of percentage of water absorbed. Moreover, with second lowest percentage of water absorbed, GM2 could as well offers good performance. In comparison of both GM2 and GM5, even though GM5 has the lowest percentage, it possessed large void that consequent to low tensile properties, while for GM2, the amount of voids present in the sample seems to be quite a number, however, the small size factor affect positively on the mechanical performance which has been proven in the previous section.

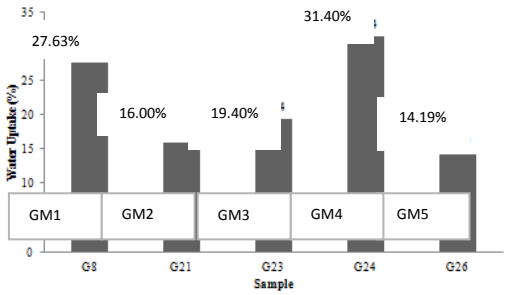

Fig. 5: Percentage of water absorbed after 24-hour immersion.

Conclusion.

Blends of thermoplastic starch and natural rubber were obtained directly from the latex and granular *Tacca leontopetaloides* starch. The natural rubber was homogenously distributed with the aids of glycerol plasticizer and rice husk silica filler. The complementation between natural rubber, Tacca starch and glycerol as a green material was responsible for a great improvement in the thermal and mechanical properties of the biopolymer. Mechanically, the adhesion between filler and GM was improved by high natural rubber content that acts as the compatibilizer. The dynamic cross-linking gives strong interface in addition to the factor of low water susceptibility. Therefore, the presence of high natural rubber content with low glycerol content has resulted in good mechanical properties and high water resistance.

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