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To cite this article: Nur Amira Sahirah Abdullah and Mohamad Kahar Ab Wahab 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **957** 012017

IOP Conf. Series: Materials Science and Engineering **957** (2020) 012017 doi:10.1088/1757-899X/957/1/012017

The Effect of Modified Jackfruit (Artocarpus Heterophyllus Lam.) Seed Starch on the Properties of Poly Lactic Acid

Nur Amira Sahirah Abdullah [1] , and *Mohamad Kahar* Ab Wahab[1,*]

[1]School of Materials Engineering, University Malaysia Perlis, 02600, Arau, Perlis, Malaysia

Abstract. This work investigates the effect of the modified jackfruit seed starch with silane coupling agent on the properties of polylactic acid (PLA). Jackruit seed starch will converted into thermoplastic like in the presence of glycerol as plasticizer. The physicochemical properties and thermal stability of the native and modified jackfruit seed starch blends with PLA were comparatively investigated. The structural changes after modification was analyzed by using Fourier Transmission Infra-red technique. Its confirmed the successful of the silane treatment from the newly peak observed at 1020 cm^{-1} and 1105 cm^{-1} for Si-O-Si and starch-O-Si bonds, respectively. For tensile strength, the value shows slightly decrese with the increasing of jackfruit seeds starch content. However the tensile properties for silane treatment shows the better improvement as compared to untreated counterpart. In the case of plasticized jackfruit seed starch, the elongation at break value increase with filler loading due to the ductile behavior of the blends system. The modification of the starch with silane coupling agent gives better interfacial adhesion between starch and PLA matrix while the glycerol gives the ductility and hydrophobicity to the starch and gives better elongation at break for the PLA/starch blends. The thermal stability of the silane treated

* Corresponding author: kaharwahab@unimap.edu.my

PLA/starch blends was also improved as compared to the native PLA/starch blends.

1 Introduction

Jackfruits (Artocarpus heterophyllus Lam.) is widely found in the tropical countries such as Malaysia, Thailand and Vietnam. The jackfruit has yellow flesh with bell shape and smooth surface seeds. Jackfruit seeds have high content of carbohydrate, protein, and starch [1-3]. The jackfruit seed starch is completely biodegradable and highly hydrophilic. Jackfruit seed starches can be modified physically or chemically to improve the physicochemical properties of the starch films. The starch can be converted into the thermoplastic starch (TPS) by addition of plasticizer. The commonly used of plasticizer in the synthesis of TPS are water, glycerol, urea, and citric acid. Other than that, the chemical modification of the jackfruit seed starch can be done by binding the hydroxyl group on the starch with other functional group to improve the hydrophobicity of the starch. The examples of the chemical that can be used in this modification are dodecenyl succinic anhydride (DSA), octenyl succinic anhydride (OSA), maleic anhydride (MA), and 3-chloropropyl trimethoxysilane [4,5]. Blending TPS with PLA is one of the approach to produce biodegradable plastics. PLA have high modulus, high strength, excellent clarity, good biocompatibility and biodegradability. The PLA have widely used in the biomedical application, and industrial packaging. The limitations of the PLA are highly in cost and brittleness [6-8]. Thus, the TPS was used in PLA matrix in order to obtain fully biodegradable composites with cost effective and improved impact resistance. However, PLA and starch are thermodynamically immiscible due to the different in hygrascopicnature. The interfacial adhesion between PLA and starch will be poor if they are blended directly. There are some modifications to improve the interfacial adhesion and mechanical properties between PLA and starch blend such as by addition of coupling agent or reactive compatibilizer. Besides, the composites are usually brittle if PLA is blended with granule starch especially at high starch conent. The plasticized starch or thermoplastic starch can be as alternative blend with PLA. In this research, the modifications of the jackfruit starch with plasticizer and silane coupling agent was focused and studied in details.

2 Experimental

2.1 Materials

Jackfruit seeds was obtained from a local market in Perlis, Malaysia and have bell shape and smooth surface. The poly (lactic acid) (PLA) was supplied by Titan Chemical, Malaysia in granular form. Analytical grade glycerol and 3-(trimethoxysilyl)propyl methacrylate (MPS) was supplied by Sigma Aldrich, Germany and used as received.

2.2 Preparation of the sample

2.2.1 Isolation of Starch (JF) from Jackfruit Seed

The jackfruit seeds were cleaned manually and the white aril was peeled off and removed. Then, the seeds will soak into the 5% concentration of NaOH to remove the brown spermoderm cover for two hours at room temperature. After two hours, the NaOH solution was removed and the seeds were rinsed with distilled water [3]. The seeds were scrubbed by using a soft brush in the tap water to remove the brown spermoderm to obtain the cotyledons of the seeds. The seeds were dried in the laboratory oven at temperature of 50ºC for 9 hours. Then, the dried seeds were sliced into small pieces and undergo grinding process by using ring mill to obtain the jackfruit seed starch in powder form. The starch powder is then dried again in the laboratory oven at temperature of 80ºC for 6 hours to remove residual water content. Lastly, the dried starch powder was sieved at 63 μm by using laboratory sieve.

2.2.2 Jackfruit Seed Starch Modification with Silane (JFS)

The jackfruit seed starch modification with silane was followed the method proposed by Kahar et al. [11].The 600 ml mixture of the ethanol/water was prepared with ratio of 80/20. The 150g of jackfruit was suspended in the mixture of ethanol and water. The 18 ml of 3 w/w% 3 -(trimethoxysilyl)propyl methacrylate (MPS) was added into the suspension of the starch and the pH was adjusted to 4 by addition of acetic acid. The mixture was stirred at room temperature for 2 hours. The MPS-modified starch was filtered and washed with ethanol to remove excess silane. The MPS-modified starch was dried in the laboratory oven at 50ºC for overnight. The MPS-modified starch was grinded and sieved at 63 μm.

2.2.3 Preparation of Modified Jackfruit Thermoplastic Starch (JFT)

Glycerol was used as a plasticizer in order to convert the granule starch into thermoplastic starch. The 97.5 g of granule starch (65 w/w%) was dry mixed with 52.5 g of glycerol (35 w/w%) at room temperature and let to overnight [9]. Then, the mixture was compounded by using heated two roll mills at temperature of 120ºC for 10 minutes.

2.2.4 Preparation of PLA/jackfruit Seed Starch Blend.

PLA/jacruit seed starch blends were prepared by using heated two roll mill at 170ºC with rotation rate of 10 rpm. Firstly, the PLA was added to the nip of the heated two roll mill and processed until it melts. Then, the JF was added and mixed with PLA until homogeneous. Then, the PLA/JF compound was undergoing hot press molding to produce a 1 mm PLA/JF sheet. The hot press molding process was take place at 170ºC for 6 minutes.

3 Characterization and Testings

The tensile testing was carried out by using an Instron machine with model 5569. The standard used for tensile testing was ASTM D638 for plastic. The cross head speed was set at 50 mm/min and the gap between upper jaw and lower jaw was set at 50mm. The tensile strength and elongation at break were measured by calculating the average values of five identical samples for each formulation. The Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the functional group present of the PLA/JF, PLA/JFT, and PLA/JFS compounds. The model of the FTIR used was Perkin-Elmer FTIR200. The sample was scanned with wavelength between 4000cm^{-1} to 40000cm^{-1} 00 The total scans used were 32 scans. The Scanning Electron Microscope (SEM), model JEOL JSM-6460LA was used to analyze the morphology of the PLA/JF, PLA/JFT, and PLA/JFS blends by observing the tensile fracture surface of the samples with the supply of accelerating voltage at 10kV. The samples were coated with platinum at about 1.5 – 3.0 nm thickness in order to prevent the electrostatic charge during the experiment. The Thermogravimetric Analysis (TGA) model Pyris Diamond, Perkin-Elmer was used to measured the weight changes as a function of temperature and time in a controlled atmosphere. The TGA and DTA curves were obtained by heating samples from the 20ºC to 700ºC at 10ºC/min under the nitrogen atmosphere.

4 Discussion

4.1 Structural analysis

For the native jackfruit seed starch spectra shown in Fig. 1, the band appear at 763 cm^{-1} indicating the C-C stretching while the C-H bending appear at 860 cm^{-1} which attributed to the vibration of starch glucosidic ring. The peak at 1020 cm^{-1} and 1079 cm^{-1} shows the C-O-H and C-O-C anhydroglucose unit while at 932 cm^{-1} represents the C-O stretching in a C-O-C bond [12]. The band at 1647 cm^{-1} originated from tightly bounded water to starch particle and those band was observed at 2931 cm^{-1} and 3394 cm^{-1} of the C-H and O-H bonds respectively. For the thermoplastic starch spectra, the peak at 2930cm^{-1} was abserved and represent the intermolecular bonds between starch and glycerol hydroxyl group [13]. This show that the glycerol was tightly bounded and trapped in the starch network during the plasticization process. The shifted this peaks to the lower wavenumber indicated the hydrogen bonding was formed between glycerol and C-OH bond in starch. The changes in starch structure after the modification with silane can be determine by formation of the Si-O-Si bond and starch-O-Si bond at the fingerprint region due to silane linkage with jackfruit seed starch. By referring to Fig. 2, the JFS reveals an absorption peak at 1019 cm^{-1} that represented to polysiloxane Si-O –Si bridge. The shoulder peak at 1105 cm^{-1} was observed as Si-O-C peak which due to the covalent bond between starch and silane. This low intensity peak also related to the residual unhydrolyzed Si–O–CH_3 groups where most of the silane had been hydrolyzed [14].

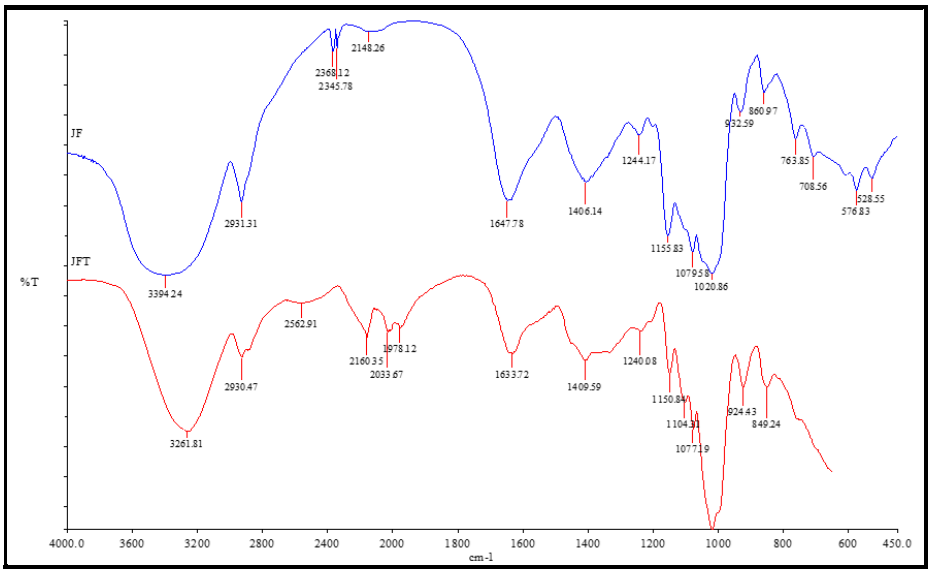


Fig. 1. FTIR spectra of JF and JFT.

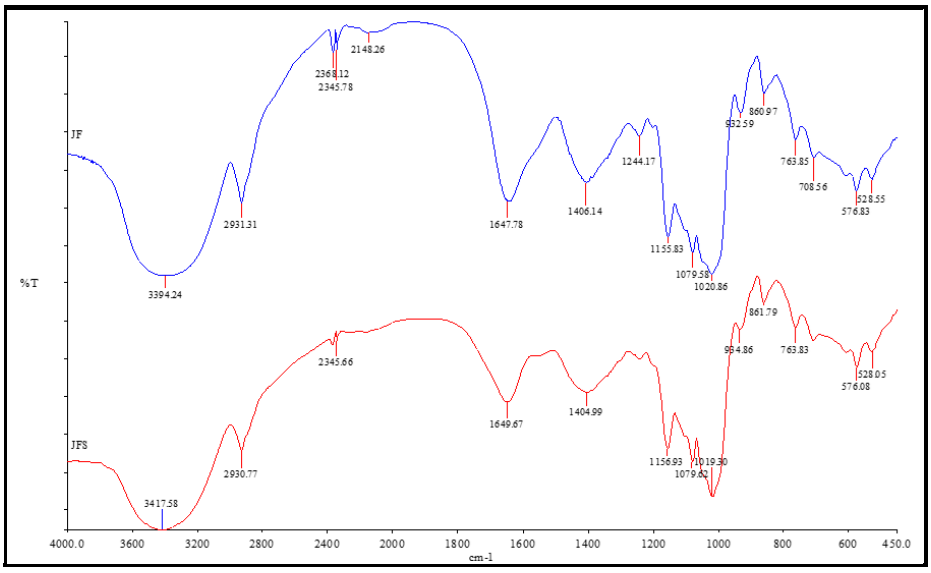


Fig. 2. FTIR spectra of JF and JFS.

4.2 Tensile properties

Fig. 3 shows the tensile strength at diferent PLA/JF, PLA/FS and PLA/JT blends ratio. For all the blend series, at 10% of jackfruit seed starch loading shows the highest tensile strength value. The increament in tensile strength was due to reinforcement effect on the PLA matrix through the mechanical interlock,which prevent the movement of PLA chains. At further jackfruit seed starch loading, the alignment of the PLA chains will be disrupt by the agglomeration of starch [15-16]. This phenomenon will lead to the tensile strength decrease as the starch content increase. The highest tensile strength recorded for PLA/JF blends at 10% jackfruit seed starch loading is 45.2 MPa and the value is decreases until 35.2 MPa for 30% of starch loading. The similar trend was observed for PLA blend with silanized jackfruit seeds starch (PLA/JFS). However, as compare to PLA/JF blend, silanized starch (PLA/JFS) shows better improvement in tensile strength. At 10% silanized jackfruit seed starch loading the tensile strength of PLA/JFS blends is 47.7 MPa. Modification with silane based, 3-(trimethoxysilyl)propyl methacrylate coupling agent can improve the interfacial adhesion between PLA matrix and starch. Good intherphases interaction allow the stress to transfer from PLA matrix into starch and prevent the crack formation at the interphase. The silanized jackfruit seed starch also improve the compatibility with PLA by attaching the hydrophobic character to starch backbone [17-18]. For PLA/JFT blends, as the JFT loading increase, the tensile strength was slightly decreases.. The highest tensile strength recorded at 5% of the JFT loading which is 39.6 MPa. In this blend system, the particulate starch was converted into the thermoplastic starch by addition of the glycerol as plasticizer. In the present of glycerol, the dispersion between JFT in PLA matrix was improved and provide some degree of reinforcement in the JFT matrix. However, the present of glyceron in JFT will soften the PLA phase and hence the tensile strength reduces as the JFT increase [19-23].

The Young's modulus of the silanized starch modification shows the highest value across all the series as shown in Fig. 3. As the starch content increases up to 10%, the Young's modulus increase due to reinforcement from incorporation of jackfruit seed starch. At further jackfruit seed starch loading, Young's modulus decreases due to the ductility of the PLA/starch blends increases. In the case of PLA/JFS blends, the silanized modification of starch shows better improvement in Young's modulus value. It's due to the silanized starch improved the interfacial adhesion between the phases and prevent the distortion of the PLA matrix. Contrary with PLA/JFT blend, the present of the glycerol as plasticizer will soften the blend and effect Young's modulus value. However, the incoprpotation of thermoplastic jackfruit seed starch in the PLA matrix, makes the compound more ductile as compared to PLA/JF and PLA/JFS. The dispersion of starch within the matrix was better due to the plasticity and the ability of JFT to flow during melt processing. The elongation at break of the PLA/JFT blends was the highst as compared to other series, which due to the flexible characteristic of the thermoplastic jackfruit seed starch.

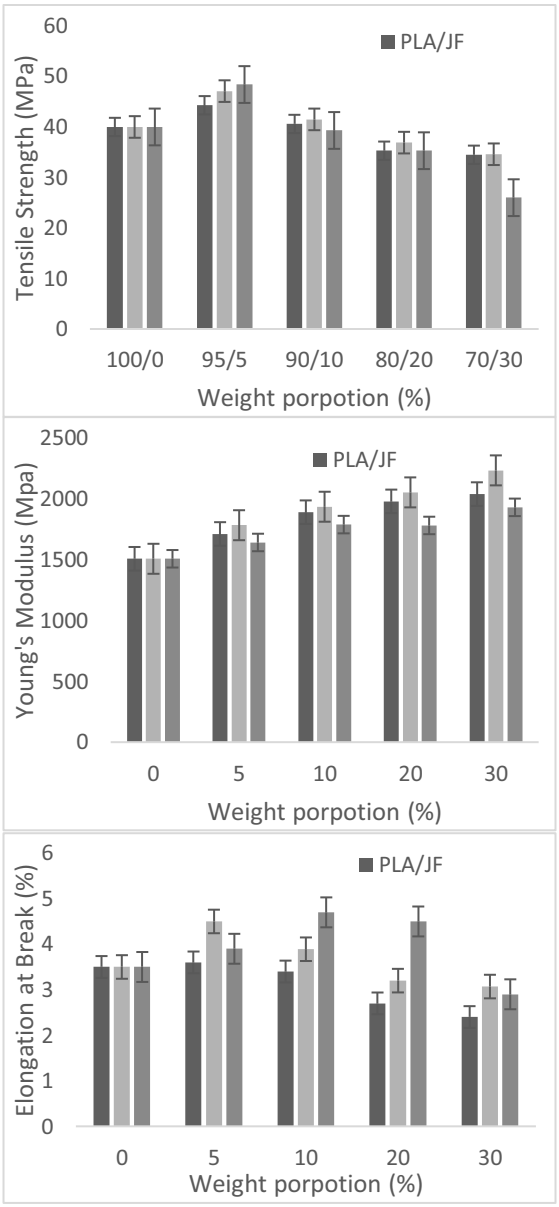
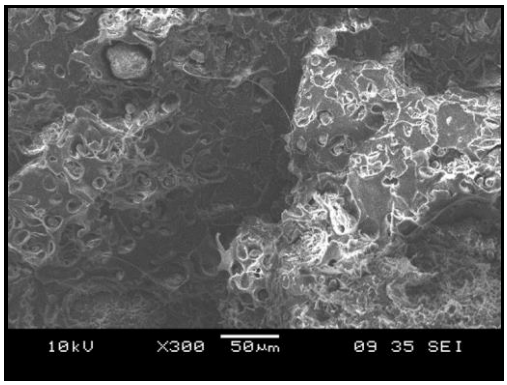


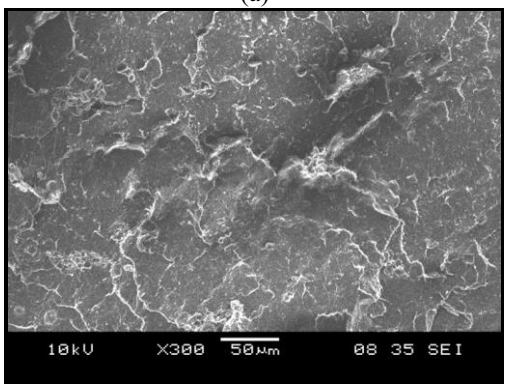
Fig.3. Tensile properties of PLA/JF, PLA/JFS and PLA/JFT blends

4.3 Morphological Study

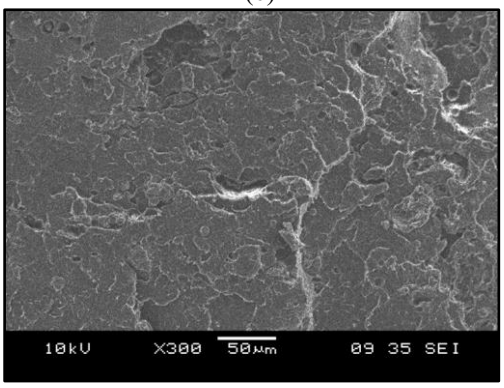
The SEM image for the PLA/JF blend at 10% of jackfruit seed starch loading is shown in Fig. 4 (a). The surface of JF ganules are quite smooth with no PLA matrix adhering to the starch particle. The size of the starch granule used was around 60 µm and remain unchanged with visible phase separation. The PLA/JF blend shows that the blend system is immiscible and incompatible due to the appearance of holes separating the starch granules and PLA matrix. As refer to the Fig. 4 (a), there is a formation of a voids along the PLA matrix that due to weak interfacial interaction between phases. Fig. 4 (b) shows the SEM image of the PLA blend with silanized jackfruit seed starch at 10% starch loading. The interfacial adhesion phases was improved and the starch particles is embedded into PLA matrix. The voids formation was reduces due to the hydrophobicity characteristic of the silanized starch. Fig. 4 (c) shows the morphology of the PLA blend with thermoplastic jackfruit seed starch at 10% of JFT loading. The JFT was observed as co-continuos phase in a PLA matrix. The disrupted the crystalline structure of starch granules allow JFT to well dispersed and existed as co-continuos phase in PLA matrix. Characteristic of plasticized starch allows JFT to elongate better with PLA matrix, which can be correlated to the better elongation at break values.



(a)



(b)



(c)

Fig. 4. Scanning electron micrograph of (a) PLA/JF blend (b) PLA/JFS blend, and (c) PLA/JFT blend at 300 X magnification.

4.4 Thermogravimetric Analysis (TGA)

The thermogravimetric analysis was used to study the thermal stability and the amount of the volatiles compounds present in the blend system. In this section, the weight loss curves and its derivatives of the blend system were investigated. The Fig. 5 (a) and (b) show the TGA curves and DTG curves of neat PLA an different PLA/jackfruit seed starch (90/10) blends system. From the Fig. 7 (a), the significant weight loss occurs at temperature range of ~50ºC-100ºC is due to the loss of moisture, at ~250ºC-320ºC is related to depolymerization of amylose and amylopectin in starch [24], and at ~320ºC-410ºC is a degradation of more thermally stable PLA phase [25]. For neat PLA, 5% weight loss appears at about 335.2ºC while the PLA/JF was occurred at about 278.8ºC. The incorporation of starch will interfere the alignment of PLA chains and therefore reduce thermal stability of the blends. For another blends series, 5% weight loss for PLA/JFS and PLA/JFT were occurred at 302.3ºC and 277.2ºC respectively. At degradation temperature of 300ºC, the PLA/JFS blend show the highest thermal stability among the blends series, which the weight loss was 4.5%, while for PLA/JF and PLA/JFT were 24.5% and 21.1%, respectively. PLA/JFS blend after silane modification show good thermal stability due to the better interfacial improvement as confirmed by SEM morphology. As refer to the Fig. 8, the maximum thermal degradation temperature for PLA/JFS blends was 347.7 °C, while for PLA/JF blends and PLA/JFT blends were slightly shift to lower temperature of 311.4ºC and 3.18.8ºC respectively. The modification of the starch with silane was improved the thermal stability of the PLA blend systems and makes heat well distributed upon thermal introduction.

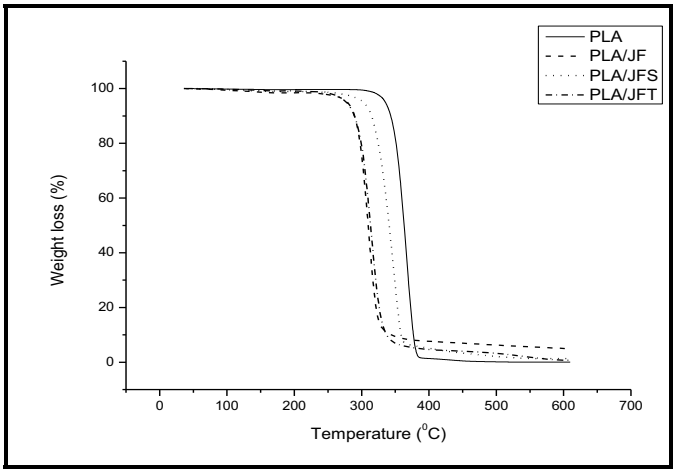


Fig. 5(a). The TGA curve of neat PLA and PLA blends of ratio 90/10.

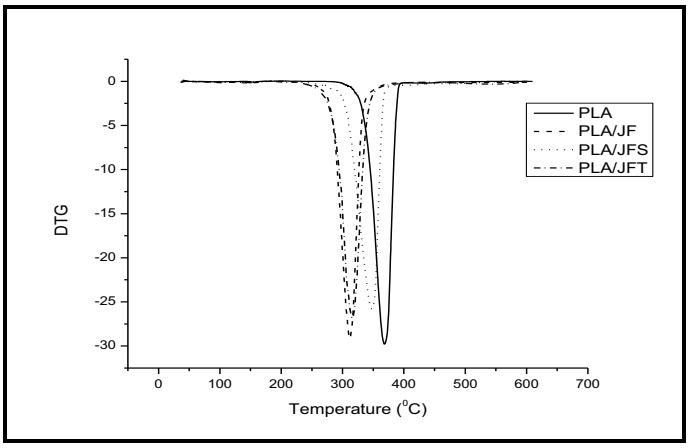


Fig. 5(b). The DTG curve of neat PLA and PLA blends of ratio 90/10.

5 Conclusions

The silane coupling agent and glycerol as plasticizer can be employed to obtain the modified jackfruit seed starch with improvement in tensile properties, interfacial interaction and thermal stability. The JFS based blend system show the highest tensile strength and Young's modulus values as compared to other series counterparts. The silanized starch also improve the compatibility and hydrophobicity with PLA matrix and resulting less void formation as proved from the SEM micrographs. The thermal stability of the blend system was also improved after jackfruit seed starch was treated with silane coupling agent. On the other hand, JFT blend systems gives the ductile behavior to the compound. The presence of the glycerol in JFT triggered the hydrogen bonding between the hydroxyl group of starch and glycerol and converting the particulate starch into a thermoplastic like. The JFT was observed as embedded phase in a PLA matrix and appeared as a co-continuous phase system. Thus, it gives homogenous morphology on the PLA/JFT blends and exhibited better elongation at break value.

The authors wish to gratefully acknowledge the School of Materials Engineering, as well as Research and Innovation Department under Universiti Malaysia Perlis and Kementerian Pengajian Tinggi Malaysia (Ref: FRGS/1/2016/TK05/UNIMAP/02/9) for supporting this research project.

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