STUDY ON A SILKWORM SILK FIBER / BIODEGRADABLE POLYMER BIOCOMPOSITE

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Abstract

Biodegradable polymeric matrix, poly(lactic acid) (PLA), was reinforced with natural animal-based fibers, silkworm silk fibers to fabricate a completely biodegradable and biocompatible biocomposite. Thermal analysis and mechanical property tests were used to determine the change of properties in comparison between pure PLA and silk/PLA biocomposites. Previous research has investigated the impact of fiber length and content upon pure polymeric materials and this topic is in need of further study and clarification. Thus, optimized fiber length and content for specific samples were used in this study for examining the relationship between silkworm silk reinforcements and PLA. This study's findings suggested that with the fiber length of 5 mm and fiber content of 5 wt%, the thermal and mechanical properties of silk/PLA biocomposites were positively enhanced when compared with pure PLA, and the findings of earlier studies indicated that silkworm silk fibers could be a potential candidate for biocomposite development.

1. Introduction

The development of biomaterials begins with those bioinert materials such as metals, ceramics and silicon etc. which are implanted permanently inside the host body without generating any response and interaction with surrounding tissues. Nevertheless, the demand of biocompatible, biodegradable and bioresorbable materials has increased drastically since the last decade. The medical applications of these biomaterials are categorized into six main fields, namely (i) tissue fixation, (ii) tissue regeneration, (iii) anti-tissue adhesion, (iv) wound closure, (v) wound dressing and (vi) drug delivery system. Consequently, a wide variety of natural and synthetic biodegradable polymers have been investigated recently for medical and pharmaceutical applications.

Natural biodegradable polymers like collagen, gelatin, chitosan and hyaluronic acid etc. have been studied for various medical applications. However, their high cost and questionable purity has limited their applications. On the contrary, synthetic biodegradable polymers, thermoplastic aliphatic poly(esters) like poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and their copolymers etc., are man-made polymers. They have a promising advantage over the natural polymers for implant developments because their favorable properties, including good biocompatibility, biodegradability, bioresorbability, and mechanical and proliferation properties, are more predictable and reproducible. Their physical and chemical properties can be easily modified and thus altering their mechanical and degradation characteristics. Additionally, synthetic polymers are generally degraded by simple hydrolysis, which is desirable as the degradation rate does not have variations from host to host, unless there are inflammations and implant degradation etc. to affect the local pH variations. They possess low or even negligible toxicity of products during in vivo degradation.

Among various synthetic biodegradable polymers, PLA is particularly offering increasing commercial interest since it is now possible to obtain high molecular weight PLA with expected lifetime by industrial technologies. Additionally, PLA can maintain its mechanical properties without rapid hydrolysis even under humid environment and thus, PLA can be a potential structural material. PLA is a highly versatile biopolymer derived from renewable resources like starch or sugar-based materials such

as corn [1]. This biodegradable polymer is alpha polyester widely used in medical applications and it has been approved by Food and Drug Administration (FDA) for implantation in human body. During biodegradation, PLA degrades into lactic acid which is finally metabolized and excreted from the host as carbon dioxide and water.

Biocomposites are mainly consisted of biopolymers accompanied by natural/bio-fibers including the plant-based and animal-based fibers. Silkworm silk fiber is one of the animal-based natural fibers which is a potential candidate for structural composites and can be used for various medical applications such as wound sutures and biomedical scaffolds. In modifying the thermal and mechanical properties of biodegradable polymers, silk-based fibers reinforced polymeric composites have emerged recently [2-7]. According to previous literatures, non-biodegradable polymeric resin like epoxy and natural or synthetic biodegradable polymers such as alginate and poly(butylene succinate) (PBS) are mainly used as matrix materials. However, little attention has been paid to thermal and mechanical properties of silkworm silk fiber/PLA biocomposites. Yet, for PLA, traditional synthetic, like glass and recycled newspaper fibers, and plant-based natural fibers, like abaca and bamboo fibers, are usually used and few investigations have evaluated the usage of animal-based natural fibers as reinforcements for this biodegradable polymeric matrix [8-11].

Experimental data from preceding studies [3,4] tend to support the idea that the use of silkworm silk fibers as reinforcements is able to enhance the mechanical properties of polymeric materials, and the researches developed the conceptual framework for silk-based polymeric composites to be a promising candidate for wide variety of structural applications. Previous researches have investigated the impact of silk fibers upon polymeric materials and gave attention to the development of fully biodegradable biocomposites. The purpose of this present study is to advance the understanding of the thermal and mechanical properties of a natural/bio-fiber reinforced biodegradable polymeric bio-composite, and a silkworm silk/PLA biocomposite will be investigated. For thermal property tests, differential scanning calorimetry (DSC), thermogravimetrical analysis (TGA) and dynamic mechanical analysis (DMA) will be used for investigating glass transition, melting and decomposition temperatures, thermal stability, and dynamic loss modulus, dynamic loss modulus and tan(δ) as a function of temperature and frequency of the silk/PLA bio-composite respectively for tackling the thermal stability problems of biodegradable polymers. Besides, the enhancement of mechanical properties of polymeric materials with the use of silk fibers is in need of further study and clarification, thus, the mechanical property tests according to the ASTM standard will be performed in order to compare the material properties between pure PLA samples and silk/PLA biocomposites. For testing and analysis, tensile and hardness test for measuring the strength and modulus will be performed. Last but not the least, the morphology of fracture surfaces of the biocomposites will be observed by imaging technique with the help of scanning electron microscope (SEM) under ambient temperature for analyzing the bonding property among silkworm silk fibers and PLA matrix.

2. Experimental Procedures

2.1 Preparation of composites

Natural tussah or raw continuous silkworm silk fibers were used as reinforcements for pure PLA to fabricate a completely biodegradable biocomposite. Silkworm silk fibers were cut gently into short fibers in the length of 5 mm in order to make sure that the fibers were not stressed plastically during the fabrication process, and 5 wt% of silk fibers were used for each set of samples according to the previous studies. The matrix used in this study was PLA which was kindly supplied by East Link Degradable Materials Ltd., Hong Kong. Before fabricating the biocomposite, silk fibers and PLA pellets first underwent a dry treatment with heat applied (80^{o}C) for 24 hours in an oven so as to remove excessive moisture. Otherwise, the properties of this kind of thermoplastic would be strongly affected due to the formation of voids after curing. In this study, a comparison was made between a pure PLA sample and a silk/PLA biocomposite with fiber contents of 5 wt%. All sets of samples were fabricated by extrusion and injection molding method to maintain consistent results. The fibers and PLA matrix were mixed at the ratio of 5:95, fed into a Hakke MiniLab twin-screw micro extruder and a uniform temperature of 183 ^{o}C was maintained at all zones inside the machine. The screw speed and the mixing duration were set to 100 rpm and 10 minutes, respectively. The first run of the extrusion was discarded and the

strands of the extrusion products were then directly collected by a pre-heated injection cylinder for further injection molding. The molten mixture was then transferred to a Thermo Hakke small scale injection-molding machine; the injection cylinder and the mold were pre-heated to the desired temperatures of 200 ^{o}C and 45 ^{o}C respectively. The resultant composite was in a dumbbell shape according to ASTM D638 for further testing.

2.2 Measurements

DSC was used to characterize materials for melting points, glass transition temperatures, and other material and material reaction characteristics such as specific heat, crystallinity, and reaction kinetics. In this study, the melting and crystallization behavior of PLA and the silk /PLA biocomposite were studied by using the Perkin-Elmer DSC7 system at ambient condition. The temperature range of the experiment was programmed to start at 25 ^{o}C and end at 300 ^{o}C at a constant scanning rate of 10 ^{o}C/min. All testing samples with sample weight of approximately 5 mg was placed and sealed into an aluminium pan, and an empty aluminium pan which has the same weight as the sample pan was used as reference. The heat flow and energy changes in the aluminium pans were recorded. By observing the difference in heat flow between the samples and the reference sample, DSC was able to measure the amount of energy absorbed or released during the samples' phase transition. Therefore, crystallization and melting temperatures could be read from the peaks as shown on the graph, and even more subtle phase changes like glass transition temperature (T_g) could be observed.

DMA is a technique in which the elastic and viscous responses of a sample under oscillating load are monitored against temperature, time or frequency where the frequency of oscillation is proportional to the modulus (stiffness) of the material. Properties obtained from DMA as a function of temperature include storage modulus (E' or G'), which is the measurement of energy stored during deformation and related to solid-like or elastic portion of the elastomer, loss modulus (E" or G"), which is the measurement of energy lost, usually as heat, during deformation and related to liquid-like or viscous portion of the elastomer, and tangent delta (tan δ), which is related to material's ability to dissipate energy in the form of heat. Elastomer melting point (T_m) and glass transition temperature (T_g) can also be determined from DMA curves. Here the Perkin Elmer Diamond DMA Lab System was set to scan thermally from 25 ^{o}C to 100 ^{o}C with a scanning rate of 2 ^{o}C/min. Sinusoidal oscillation of 1 Hz was selected. According to the specifications provided, for a dual-cantilever bending test, the sample was processed to 50 mm in length, 5 mm in width and 1.5 mm in thickness with both ends clamped. A load was applied in the middle of the sample.

Thermal stability of both the pure PLA sample and the silk/PLA biocomposite were revealed by making use of the Setaram Labsys TG-DTA/DSC (the accuracy was ±1 μg) system at ambient condition. The temperature was set to start at 25 ^{o}C and end at 500 ^{o}C with the temperature scanning rate of 10 ^{o}C/min, and air flow rate was set to be around 400 cc/min.

Tensile and hardness tests were performed to examine the mechanical properties of pure PLA samples and silk/PLA biocomposites. The tensile test was carried out according to the ASTM standard by using the 50kN MTS Alliance RT-50 tensile machine and extensometer. In order to maintain accuracy of results, all specimens were molded into a dumbbell shape and underwent the same ambient testing conditions. The span length was 50 mm, and crosshead speed with a loading rate of 2 mm/min was used. 10 samples for each of the pure PLA sample and 5 wt% silk/PLA biocomposites were tested for averaging the results.

Hardness test was performed with the use of the Vickers hardness tester (Future-tech FM series). The loading force and dwelling time were set as 100 gram force and 15 seconds respectively. Since the injection molded samples were both sided polished and flattened, further surface finishing processes could be neglected. Samples were randomly selected, and 5 points were dwelled on each sample for averaging the results to maintain accuracy.

After the thermal and mechanical property tests, microscopic analysis with the help of Leica Stereoscan 440 scanning electron microscope (SEM) was conducted on fracture surface of the samples to examine the failure surface structure and failure behavior induced by the tensile test. Bonding between fibers and matrix could be observed, and micro structure inside the silkworm silk fibers and the biocomposites could be determined. Testing was performed at room temperature with tungsten

filament, and an accelerating voltage of 20 kV was used to capture SEM images for both of the pure PLA samples and the 5 wt% silk/PLA biocomposites. All specimens were viewed perpendicular to the fractured surface.

3. Results and Discussion

3.1 Crystallization and melting behavior of PLA and silk/PLA biocomposite

According to literature reference [12], assuming that PLA is purely crystalline, the value of melting enthalpy of PLA is approximately 93.7 J/g, so the degree of crystallinity (*X*%) in the biocomposite can be obtained by:

$$X\% = \Delta H_m / \Delta H_{mo} \times 100\%, \quad (1)$$

in which ΔH_m is the measured melting enthalpy and ΔH_{mo} is the melting enthalpy value of the purely crystalline sample. All the measured results from DSC testing were summarized in Table 1, the values of T_g for pure PLA sample and 5 wt% silk/PLA biocomposite were 58.9 ^oC and 64.4 ^oC respectively, with an increment of 9.3 %. For T_m and ΔH_m, both of the pure PLA sample and the silk/PLA biocomposite were around 170 ^oC and 35 J/g respectively, and they were quite close to each other, whereas for the crystallization temperature (T_c) and crystallization enthalpy (ΔH_c), the values decreased with the addition of silk fiber reinforcements, and the decrements were dropped by 14 ^oC and 15 J/g respectively. Moreover, the degree of crystallinity increased slightly in the presence of silk fibers, and the value was about 38 %.

Table 1. Thermal properties of pure PLA sample and 5wt% silk/PLA biocomposite by the use of DSC.

Sample / Biocomposite	T_g (^oC)	T_c (^oC)	T_m (^oC)	ΔH_c (J/g)	ΔH_m (J/g)	*X*%
Pure PLA	58.9	114.0	171.8	34.5	35.4	37.8
5wt% silk/PLA	64.4	100.2	168.4	19.9	35.7	38.1

Two main factors control the crystallization of polymeric composite systems: (i) the additives hinder the migration and diffusion of polymer molecular chains to the surface of the growing polymer crystal in the composites, thus providing a negative effect on polymer crystallization which results in a decrease in the T_c; (ii) the additives have a nucleating effect which gives a positive effect on polymer crystallization and an increase in T_c. However, in this case, the T_c of the silk/PLA biocomposite dropped by 14 ^oC. It may be concluded that in the presence of silk fibers, the viscosity of the composite mixture increased, which hindered the migration and diffusion of PLA molecular chains in the biocomposite.

3.2 Dynamic Mechanical Properties

As shown in Fig. 1., the storage modulus against temperature, E', of the silk fiber biocomposite was higher than that of the pure PLA sample. The modulus increased in the presence of silk fibers, which can be concluded as a combined effect of the fibers embedded in a viscoelastic matrix and the mechanical limitation introduced by the fibers. At high concentration, the fibers reduced the mobility and deformation of the matrix, and in this case, the stress could be transferred from the PLA matrix to the silk fiber reinforcements [13]. Also, it could be observed that the E' value of both the pure PLA sample and the silk/PLA biocomposite dropped drastically between 53 ^oC and 67 ^oC which were their glass transition regions. However, in this glassy zone, the contribution of fiber stiffness to the composite modulus was minimal. Normally, short fiber composite properties are governed by the fiber orientation, fiber length distribution, fiber dispersion and fiber-matrix adhesion. When hydrophilic silk fibers were mixed with hydrophobic PLA matrix, even using the extrusion and injection machine with heat and pressure applied, fiber dispersion would be a serious problem to deal with; but still, the stiffness of the biocomposite was increased as E' increased in this study.

Fig. 2. compared the loss modulus as a function of temperature for both the pure PLA sample and the silk/PLA biocomposite. Comparing the E" peaks of the two different samples, the T_g of the silk/PLA biocomposite was slightly shifted to higher temperature with a broader range of the transition region than the pure PLA sample. As the loss factors are sensitive to molecular motions, it could mean that the mobility of the polymer molecular chains decreased as the chains were hindered by the silk fiber reinforcements and led to the shift of T_g. This might be a trend that as silk fiber content increased, the mobility of polymer chains decreased, and T_g increased subsequently.

According to Fig. 3., tangent delta as a function of temperature for both the pure PLA sample and the

silk/PLA biocomposite, from the relationship between E', E" and tan δ [14], can be calculated as:

$$\tan \delta = E''/ E'. \quad (2)$$

Tan δ decreased as seen from the graph in the presence of silk fibers. This might be again due to the decrease of the mobility of polymer molecular chains as hindered by the reinforcements, which led to a reduction of height and sharpness of the peak in the curves. In addition, damping in the transition region measured imperfection in the elasticity, and some of the energy used to deform the material was directly dissipated into heat. Thus, the mechanical loss that overcame the friction of intermolecular chain was reduced with silk fiber additives [15,16]. It was also claimed in another literature that the reduction in tan δ denoted the improvement in hysteresis of the system and a reduction in internal friction [17].

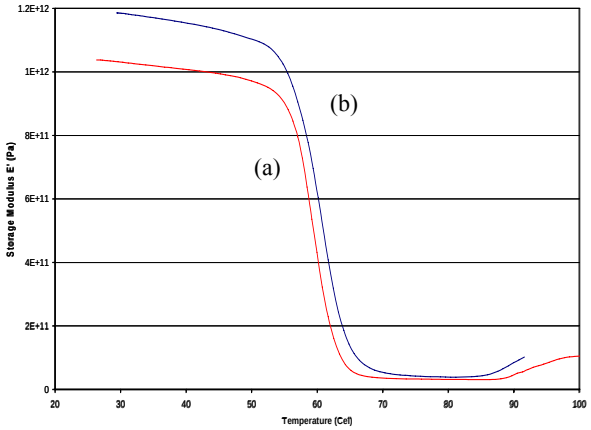

Fig. 1. Storage modulus as a function of temperature of (a) pure PLA sample; (b) 5 wt% silk/PLA biocomposite

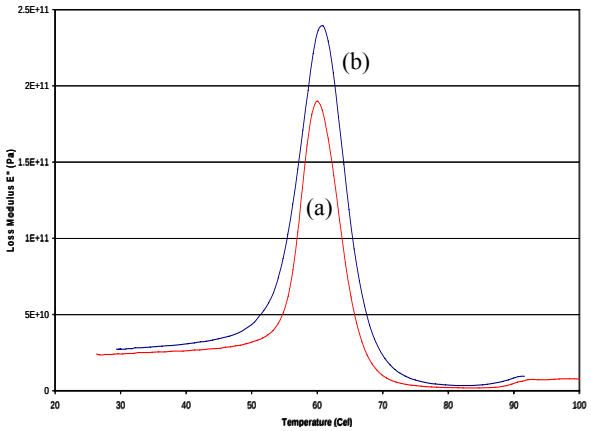

Fig. 2. Loss modulus as a function of temperature of (a) pure PLA sample; (b) 5 wt% silk/PLA biocomposite

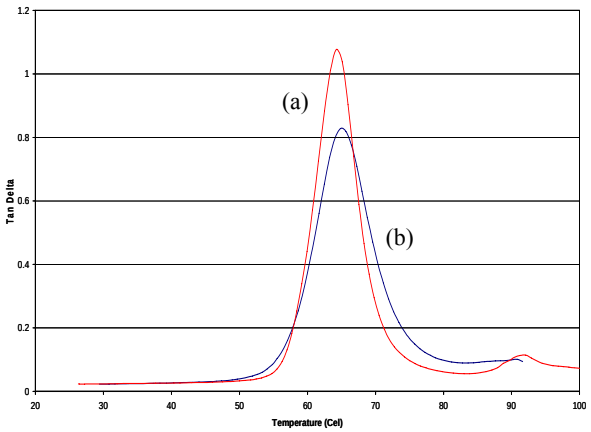

Fig. 3. Tangent delta as a function of temperature of (a) pure PLA sample; (b) 5 wt% silk/PLA biocomposite

3.3 Thermogravimetry

From TGA testing, thermogravimetric (TG) curves and derivative thermogravimetry (DTG) curves as a function of temperature of both the pure PLA sample and the silk/PLA biocomposite were obtained and shown in Fig. 4. and 5. The TG curves indicated thermal stability of the materials, whereas the DTG curves showed the decomposition temperature of the materials. Generally speaking, silk fibers were degraded through three main stages: (i) starting from 52 ^{o}C, the absorbed moisture released from the silk fibers; (ii) a second transition, from 265 ^{o}C to 350 ^{o}C, the silk fibers underwent degradation; and (iii) from 350 ^{o}C onwards, the silk fibers started to decompose. According to the two figures, both the pure PLA sample and the silk/PLA biocomposite showed very similar results and the data of the curves were quite close to each other. In the TG graph, it could be observed that for both the pure PLA sample and the silk/PLA biocomposite, the weight percentage dropped significantly starting from 300 ^{o}C, which was mainly due to the degradation of the materials. In addition, another transition started at around 360 ^{o}C when the decomposition of the materials started. In DTG graph, a gentle declination started at around 270 ^{o}C, which was the same reason for the start of the degradation of the materials. A peak appeared at around 350 ^{o}C for both pure PLA sample and 5 wt% silk/PLA biocomposite, which was the decomposition region of the materials, and that was consistent with the results obtained by the DSC analysis.

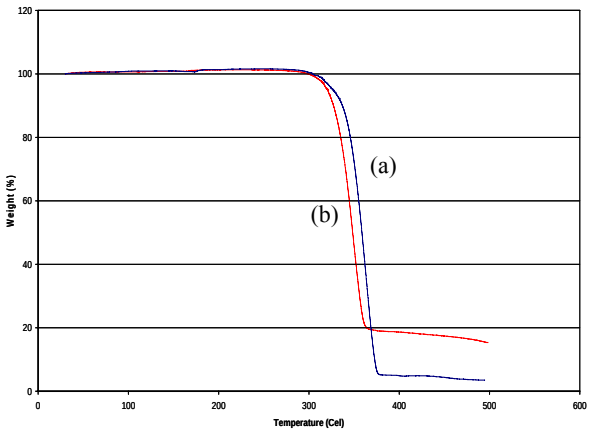

Fig. 4. Thermogravimetric curves as a function of temperature of (a) pure PLA sample; (b) 5 wt% silk/PLA biocomposite

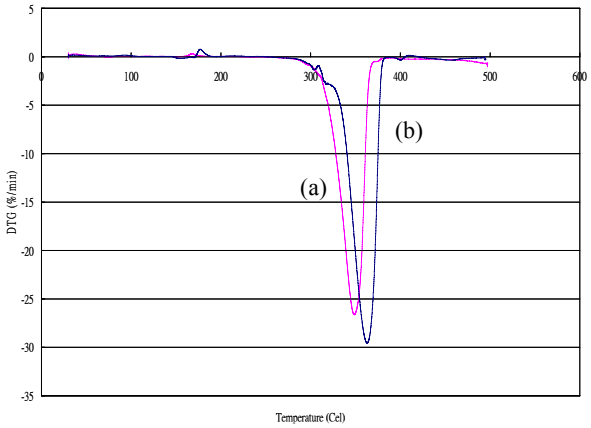

Fig. 5. Derivative thermogravimetry curves as a function of temperature of (a) pure PLA sample; (b) 5 wt% silk/PLA biocomposite

3.4 Tensile Test

Mechanical properties of pure PLA samples and 5 wt% silk/PLA biocomposites were compared by making use of the tensile and hardness tests. Sufficient amount of specimens were measured according to ASTM standard, and it was found that the results obtained were consistent and could be reproduced well. The stress-strain characteristics of the two different composition samples, including peak stress, strain percentage at break and modulus of elasticity, were listed in Table 2. The tensile strength and the strain percentage at break of the pure PLA samples were about 65 MPa and 4.7% respectively; whereas for the 5 wt% silk/PLA biocomposites the measured results were about 61 MPa and 4.6 % respectively. The elastic modulus of the pure PLA samples and the 5 wt% silk/PLA biocomposites were 1.833 GPa and 2.439 GPa respectively. As seen from the peak stress and the strain percentage at break, tensile strength and ductility of the silk/PLA biocomposites were slightly lower than that of the pure PLA samples. However, for the modulus of elasticity of the biocomposites, an increment of up to 33 % was obtained. It means that the stiffness of the silk/PLA biocomposite was much higher than that of the pure PLA sample, and the biocomposite behaved more brittle while the pure PLA sample was relatively ductile. These findings could be explained by the fractured morphology of the microstructures inside the samples, which were observed by using the SEM.

Table 2. Tensile strength, ductility and modulus of elasticity of pure PLA samples and 5 wt% silk/PLA biocomposites

Samples	Peak Stress (MPa)	Strain percentage at break (%)	Modulus of elasticity (GPa)
Pure PLA	65.15	4.675	1.833
5 wt% silk/PLA	61.25	4.575	2.439

3.5 Hardness Test

Vickers hardness test was performed to determine the hardness of pure PLA samples and 5 wt% silk/PLA biocomposites. After averaging the results, the hardness of the pure PLA samples was about 17 Hv, whereas the hardness of the 5 wt% silk/PLA biocomposites was about 19 Hv. The yield strength of the materials could be approximated by Eq. 3, with c being a constant determined by geometrical factors which is usually ranged between 2 and 4. The results obtained from tensile test showed that the yield strength of the pure PLA samples and the 5 wt% silk/PLA biocomposites were consistent with the results obtained from the Vickers hardness test, as

$$Hv = c\sigma. \quad (3)$$

There was an increment of about 12 % for the hardness between the two different set of specimens. Thus, the hardness increased as the PLA was reinforced with the silkworm silk fibers, and the overall mechanical properties of the silk/PLA biocomposites were enhanced.

3.6 SEM

Failure surface structure and failure behavior of samples were studied with the use of SEM. SEM micrographs of the fracture surface due to the tensile test of the pure PLA samples, the 5 wt% silk/PLA biocomposites and the silkworm silk fiber reinforced in the biocomposites were shown in Fig. 6., 7. and 8. SEM micrographs of the pure PLA samples (Fig. 6.) illustrated the topography of the sample. As observed from the micrographs, the topography of the pure PLA sample was relatively smooth compared to that of the biocomposites. As seen in Fig. 7., the 5 wt% silk/PLA biocomposites underwent a brittle nature and a rougher surface was obtained during the tensile test. Pullout situations of the silkworm silk fibers were not as serious as those hand-made composites, and the silkworm silk fibers were covered by a thin layer of matrix linking the fiber surface to the matrix as seen in Fig. 8. Therefore, stress could be transferred from the matrix to the fibers easier, which enhanced the mechanical properties. Although it was difficult to achieve a well dispersion of the fibers in the polymeric matrix, a considerable improvement of adhesion at the interface of the fibers and the matrix could be observed when compared to previous studies, because different composite fabrication processes were used. In addition, the fibers were dispersed as micro-pins, interlocked with the matrix, and induced a great reduction of micro voids, which might be caused by moisture absorption and air permeation during the fabrication process.

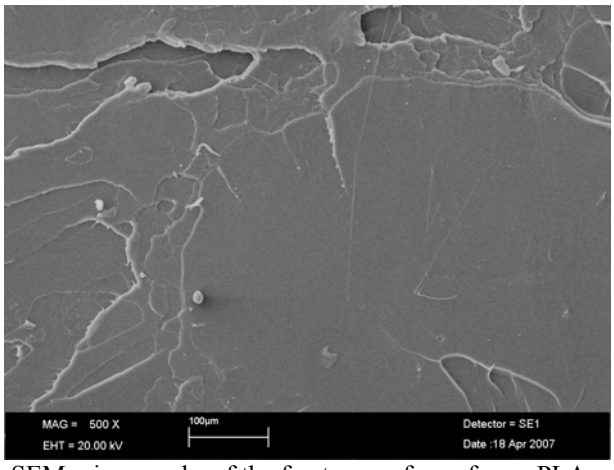

Fig. 6. SEM micrographs of the fracture surface of pure PLA samples

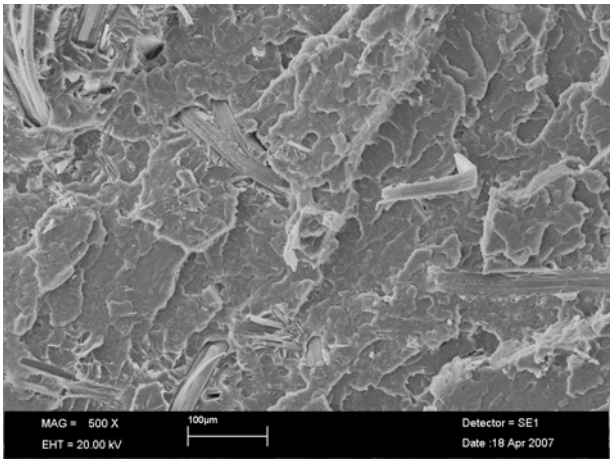

Fig. 7. SEM micrographs of the fracture surface of 5 wt% silk/PLA biocomposites

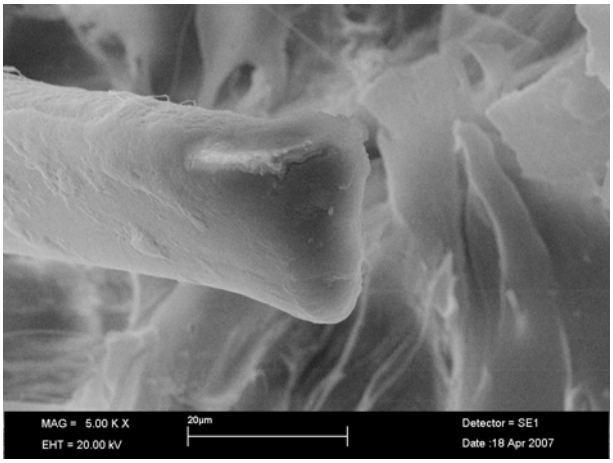

Fig. 8. SEM micrographs of the fracture surface of silkworm silk fiber in 5 wt% silk/PLA biocomposites

4. Conclusions

In this study, thermal and mechanical properties of both of pure PLA samples and 5 wt% silk/PLA biocomposites were compared. Although the silkworm silk reinforcements hindered the mobility of the PLA molecular chains in the biocomposite, which induced a negative effect on polymer crystallization and a decrement in crystallization temperature, the presence of these reinforcements enhanced the stiffness of the PLA sample as the storage modulus of the biocomposite increased desirably. The thermal stability of the biocomposite was improved as the glass transition temperature and the loss modulus as a function of temperature curves were increased, which were reflected by DSC and DMA results. Moreover, for the tangent delta as a function of temperature graph, the peak of the tan gent delta of the biocomposites had a large decrement as compared to pure PLA samples, and it could be claimed as an improvement in hysteresis of the system and a reduction in internal friction. Increment of the storage modulus (stiffness) and decrement of the tangent delta values demonstrated the reinforcing effect of silkworm silk fibers on PLA matrix.

On the other hand, the mechanical properties were investigated with tensile and hardness tests. Compared to the pure PLA samples, stiffness and hardness of the biocomposites were improved as the tensile modulus and the hardness were increased by up to 33 % and 12 % respectively. Last but not the least, according to the SEM micrographs, it was observed that the silk/PLA biocomposites exhibited a brittle nature, and silk fibers were dispersed better than in previous studies. Fibers were dispersed as micro-pins which interlocked with the PLA matrix and micro voids were greatly reduced at the fracture surface induced by the tensile test. Further study of silk/PLA biocomposites should be made in order to enhance the interfacial bonding between the PLA and the silk fiber reinforcements, to introduce better dispersion processing methodologies of silk fibers on PLA matrix, and to assess the biodegradability of this type of potential candidate for clinical applications.

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