



RESEARCH ARTICLE

FABRICATION AND THERMO-MECHANICAL CHARACTERISTICS OF PHBV/LATEX/VEGETABLE OIL COMPOSITES-MODIFYING ON BIOCOMPOSITES

Agung Kristanto^{1&3}, Manida Swangnetr Neubert^{2 &3}, Sarunya Promkotra^{4*}, Weerapat Sessomboon¹

¹Department of Industrial Engineering, Faculty of Engineering, Khon Kaen University, Khon Kaen, Thailand

²Program of Production Technology, Faculty of Technology, Khon Kaen University, Khon Kaen, Thailand

³Research Center in Back, Neck, Other Joint Pain and Human Performance(BNOJPH), Khon Kaen University, 40002, Thailand

⁴Department of Geotechnology, Faculty of Technology, Khon Kaen University, Khon Kaen, Thailand

*Corresponding Author Email: sarunya@kku.ac.th

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ARTICLE DETAILS

ABSTRACT

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Polyhydroxybutyrate-co-hydroxyvalerate (PHBV, P) and natural latex (L) are mixed together to improve biostructures due to very stiff PHBV and high resilient natural latex. Another raw material added in PHBV/L mixtures is a vegetable oil which is vary between virgin coconut oil (VC) and cooking coconut oil (CC). Then, the three mixtures are known for P-L-C biocomposites. These three different components among PHBV, natural latex, and the coconut oil are considered to obtain their proper mechanical properties. The 2% and 3% (w/v) of PHBV concentrations (2P, 3P) in chloroform are started as the main component, and mixed to natural latex (L) and coconut oil (VC or CC) as the blended films in the ratio of 12:8:1, 10:10:1, 8:12:1, and compared to 6:4:1, 5:5:1, 4:6:1, respectively. The blends are specified the thermal property by the differential scanning calorimetry and also distinguished with their crystallinity. Besides, they are also characterized the tensile strength by universal testing machine. The degree of crystallinity is inversely proportional to the melting temperature particularly for 3Px-Lx-C1. The 3% w/v of PHBV-Latex-Coconut oil blends presents higher melting temperature than the 2% w/v of PHBV-Latex-Coconut oil mixtures. Adding coconut oil mixes show a lower melting temperature at 166-167°C when is compared to the mixture without coconut oil at 168-169°C. The virgin coconut oil mixes specify no inconsistency of the melting temperature, enthalpy, and degree of crystallinity. The addition of the coconut oil can diminish the 50% of tensile strength and the 6-7% of tensile modulus. The cooking coconut oil added in the 2% w/v PHBV-Latex matrix affects a 10% increase in tensile modulus related to the 3% w/v PHBV-Latex matrix. The appearance of the coconut oil in the blend is suitable for conformity of plastic deformation.

KEYWORDS

Mechanical characteristics, Tensile strength, Latex, PHBV, Coconut Oil, Biocomposite.

1. INTRODUCTION

Bio-based complexes are extremely experimented in recent years due to their certain properties and obviously explicit environmental influence. Polyhydroxylalkanoates (PHAs) are one of biodegradable polymers on aliphatic polyesters, produced organically from microbial activity on sugar-based medium. A type of polyhydroxybutyrate-co-hydroxyvalerate (PHBV) is a distinctive instance of PHAs, with decent biodegradability fabricating by many microorganisms [1]. Crystalline configurations of PHBV chains and co- monomer contributions are statistically arbitrary forms. The HV contents of 3HB (hydroxybutyrate) and 3HV (hydroxyvalerate) copolymers provide their property changes. The major concerning properties of PHBV biopolymers are basically rigid, brittle and low resilient materials which are unapproachability of outstanding mechanical property [2]. To improve their mechanical properties, various revision has been suggested and processed of PHBV and mixed with natural rubber latex, for example the chemical variation and physical mingling. The mechanical examinations indicate complex specific configurations of mechanical properties of the PHBV/Latex blends which higher PHBV content signifies the better elastic modulus [3]. The outcomes of mechanical and thermal properties express that the blended PHBV are capable to develop their properties by more elasticity and broad range of temperature. Moreover, the biodegradable PHBV is mixed with a green tea polyphenol (TP) as toughened. Mechanical and thermal properties of composites show that PHBV/TP matrix is able to improve the toughness of the composites [4]. The results of the differential scanning calorimetric (DSC) present a single glass transition and an inferior melting temperature. Several matters based on PHBV are improved

their properties by blending to other biodegradable polymers, such as natural rubber, epoxide natural rubber [5], polybutylene adipate-co-terephthalate [6].

Natural latex rubber is a material that has gained much scientific attention due to the present extensive utilization of non-renewable supplies and the naturally toxic discarding required for conventional polymers. Property of natural rubber presents a soft and high elastic material. Some nanoparticles are used as filler to improve strength and ultimate deformation. The mainly important of rubber is the enhanced reinforcement by stiff objects, such as dispersed additives or phase-separated organic parts [7]. Compatibility of the rubber blended to other components contributes extra interrelated phases, which can develop the properties. Block copolymers are useful for congruent phase-segregated combinations, by diminishing the surface tension [8] and instantaneously increasing the strength of the interfacial sections [9-10]. Concentrated researches related to filler types is to develop the mechanical properties of elastomeric materials as natural rubber, such as carbon nanotubes, carbon black, and some clays [11-12]. Another substance for blending in natural rubber is vegetable oils. They have plenty of free fatty acids which are useful for mixing in rubber compounds. Some vegetable oils act as a vulcanizing agent in carboxylate nitrile rubber blends [13]. To develop their mechanical properties and processability, linseed oil is beneficial additive in rubber compound. Soybean oil is exploited as a plasticizer in natural rubber [14]. Also, castor oil is acted as a plasticizer in nitrocellulose and rubbers containing styrene. Basically, vegetable oils behave as a coupling agent for development of rubber-filler interaction in carbon black [15].

One of vegetable oils is coconut oil which contains high saturated fat content or fatty acid, known as medium chain triglycerides, such as lauric acid, capric acid, caprylic acid, and caproic acid. However, this coconut oil is still contained a small amount of long chain triglycerides. To improve physical properties of PHBV and natural latex blends, coconut oil is selected to be an additive in a natural latex composition containing the oil-extended latex rubber as a component. The purpose of this research is to provide a coconut oil as a plasticizer- increased latex containing PHBV component. The PHBV concentration is controlled in two series of 2% and 3% w/v in chloroform blending with fresh creamy latex. The coconut oil is compared to both virgin coconut oil and cooking coconut oil. This biopolymer product is intended to reveal the mechanical characteristics of the blends related on its thermal property, focusing the attention on vegetable oil in terms of thermo-mechanical properties.

2. MATERIALS AND METHODS

Powder PHBV (trade name ENMATY1000), commercial grade, is provided from Ningbo Tianan Biologic Material Co. Ltd., China. It dissolves in chloroform (A.R. grade) at 2% and 3% w/v around 4 hr and controls

temperature at 65-70°C. This PHBV solution (P) is ready to mix with other two components, creamy latex and coconut oil. The natural latex (L) is supplied by Rubber Authority of Thailand (Khon Kaen Branch) where is cultivated from the rubber tree (*Hevea brasiliensis*) in the northeast of Thailand. The last component is coconut oil, commercial grade, and acquired from a local market. Two different types of coconut oil (C) are produced in Thailand and varied in this experiment as a plasticizer. They are virgin coconut oil (VC) and cooking coconut oil (CC). The total fat and saturated fat in the virgin coconut oil are 18% and 55%, respectively. However, the total fat in the cooking coconut oil is 18%, and no saturated fat in the portion.

The PHBV solutions in different concentration of 2% and 3% w/v (2P, 3P) are first agitated with coconut oil at room temperature. Subsequently, these mixtures of PHBV and coconut oil are vigorously blended with the natural latex (L) in three different portions and controlled the temperature at 50°C during mixing. Only the three different ratios of PHBV-Latex-Coconut oil, compared to the two series of 12:8:1, 10:10:1, 8:12:1, and 6:4:1, 5:5:1, 4:6:1, are produced and examined for thermo-mechanical test (Table 1). After energetic blending, shaping biopolymeric film with extruder allows a dried sheet at 50°C for 3 days in the oven. Thermal characteristics of these biopolymer products are examined by the differential scanning calorimetry (DSC), NETZSCH DSC 214 Polyma, Germany, based on ASTM E794 - 06 (Standard Test Method for Melting and Crystallization Temperatures by Thermal Analysis). The DSC results

Table 1: Thermal property of PHBV-Latex-Vegetable oil composite which vegetable oil is virgin coconut oil (VC) and cooking coconut oil (CC) (Remark: T_m is melting temperature.)

Item	PHBV-L-C (2% w/v)	T _m (°C)	Enthalpy (ΔH) (J/g)	Crystallinity (%)	PHBV-L-C (3% w/v)	T _m (°C)	Enthalpy (ΔH) (J/g)	Crystallinity (%)
1	2P3-L2	169.0	3.39	6.12	3P3-L2	168.9	6.81	12.29
2	2P1-L1	167.5	3.54	6.39	3P1-L1	167.6	4.74	8.56
3	2P2-L3	167.8	3.81	6.88	3P2-L3	167.8	6.05	10.92
4	2P12-L8-VC1	167.3	3.64	6.57	3P12-L8-VC1	167.5	5.76	10.40
5	2P10-L10-VC1	167.6	3.58	6.46	3P10-L10-VC1	167.6	5.23	9.44
6	2P8-L12-VC1	167.8	3.12	5.63	3P8-L12-VC1	167.6	3.90	7.04
7	2P6-L4-VC1	167.6	4.69	8.47	3P6-L4-VC1	166.9	4.15	7.49
8	2P5-L5-VC1	167.6	6.12	11.05	3P5-L5-VC1	165.9	4.46	8.05
9	2P4-L6-VC1	167.2	1.60	2.89	3P4-L6-VC1	166.4	3.35	6.05
10	2P12-L8-CC1	166.8	3.92	7.08	3P12-L8-CC1	167.0	6.08	10.97
11	2P10-L10-CC1	167.3	3.79	6.84	3P10-L10-CC1	167.2	5.65	10.20
12	2P8-L12-CC1	166.9	3.41	6.16	3P8-L12-CC1	166.4	5.42	9.78
13	2P6-L4-CC1	167.1	2.25	4.06	3P6-L4-CC1	166.5	5.58	10.07
14	2P5-L5-CC1	166.9	2.82	5.09	3P5-L5-CC1	166.0	5.40	9.75
15	2P4-L6-CC1	167.6	2.74	4.95	3P4-L6-CC1	166.3	3.77	6.81
16	PHBV	175.0	55.40					
17	Rubber	204.1	9.12					

The area under a main peak is the enthalpy. The results of crystallinities (%) for the blend products are summarized in Table 1. The comprehension of the degree of crystallinity is significant to reveal the affected physical properties, for instance melting temperature, elastic modulus, and density. Mostly these appearances of crystallinity provide a primary property to predict other physical properties. Overall degree of crystallinity for the 3% w/v of PHBV blends (3Px-Lx-Cx) presents higher than the 2% w/v of PHBV blends (2Px-Lx-Cx), except for the series of 2P6-L4-VC1 and 2P5-L5-VC1

reveal certain aspects of melting temperature (T_m), enthalpy (ΔH), and crystallinity (%).

Mechanical test is performed by using Universal Testing Machine (UTM, Instron 5567A). Specimen size measuring refers to ASTM D882-10 with a rectangular shape of specimens, dimension specifications as 100 mm in total length, 20 mm width, and 50 mm in gauge length (benchmark). Thickness of the specimen is closely to 1.0 mm which is measured by a vernier caliper. Three specimens of each composite film are tested for calculating the average of a set of tensile data. Before the test, the specimens are held tightly with pneumatic grips and controlled a crosshead speed of 5 mm/min.

3. RESULTS AND DISCUSSION

The PHBV has been mixed with natural latex and vegetable oil that affords reinforcing appearance for the intention of formulating value-added outcomes. The challenge to discover proper blend affiliates for PHBV is to develop PHBV properties. The formulation of the blends is presented in Table 1. Three components with several concentrations and the mixing ratios are varied in two series, entirely compared their physical properties together.

3.1 Differential Scanning Calorimetry (DSC)

The biopolymer films are examined for thermal and mechanical properties by the differential scanning calorimetry (DSC) which specifies a prompt method for verifying polymer crystallinity depended on the heat involved to their melts. This technique measures heat flow in/out of a biopolymer as a function of temperature. Thermograms attained from the first heating scan for the PHBV-Latex biocomposites (P-L), and PHBV-Latex-Coconut oil (P-L-C) blends are shown in Figure 1. Melting temperature (T_m) and enthalpy are obtained from the first heating scan. However, the degree of crystallinity of blends is calculated by computing the heat associated with melting (fusion) of these composites. This heat is stated as crystallinity in percent by normalizing with respect to the fusion heat of a 100 % PHBV crystalline sample, as indicated in Equation (1).

$$\text{Degree of crystallinity} = (\Delta H_f - \Delta H_c) / \Delta H_{f,100\%} \times 100\% \quad (1)$$

where ΔH_f is the enthalpy of melting, ΔH_c is the enthalpy of crystallization, and ΔH_{f,100%} is the enthalpy of melting for a fully PHBV crystalline polymer based upon 55.40 J/g.

(Figure 2). The coconut oil mixes show a lower melting temperature (166-167°C) compared to the mixture without coconut oil (xPx-Lx) (168-169°C). Moreover, the virgin coconut oil mixes indicate the physical properties of a poor inconsistency of T_m, enthalpy, and degree of crystallinity. Melting points of 3Px-Lx-C1, in which increase both virgin- and cooking coconut oil, obviously decrease in the range of 1.0-1.5°C, as indicated in Figure 3.

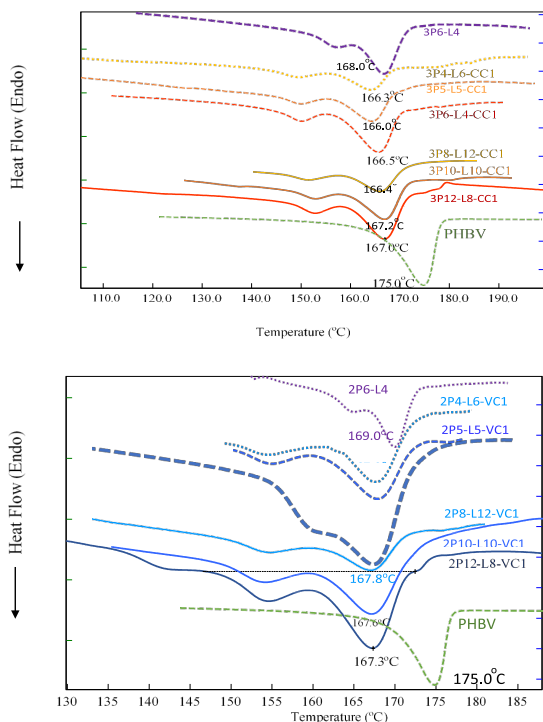


Figure 1: Melting endotherms for biopolymer films in different compositions of PHBV-Latex-Coconut oil (Px-Lx-Cx) by vary the concentrations of PHBV (2%, 3% w/v) and the ratio of PHBV, latex, and both virgin coconut oil (VC) and cooking coconut oil (CC), corresponding to Table 1

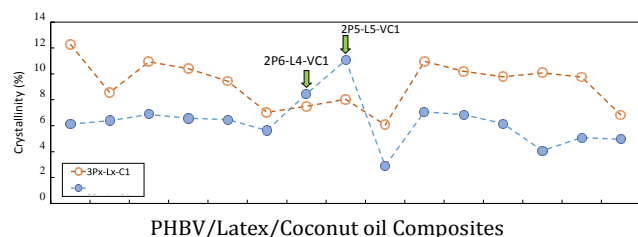


Figure 2: Crystallinity (%) related to the composite materials of PHBV-Latex-Coconut oil in different mixing ratio, corresponding to Table 1

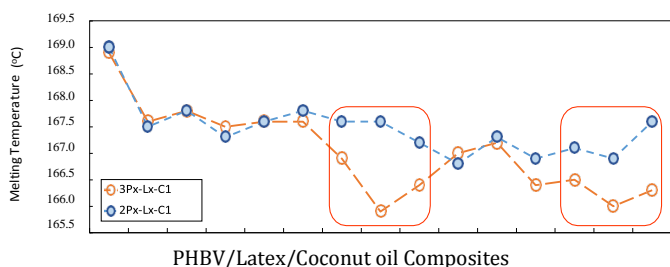


Figure 3: Melting temperature related to the composite materials of PHBV-Latex-Coconut oil in different mixing ratio, corresponding to Table 1

3.2 Tensile Testing

The tensile stress as a function of the tensile strain of the 2-3% w/v PHBV-Latex composite made without coconut oil, 2Px-Lx and 3Px-Lx, shows the ultimate strengths of 130-160 KPa and 60-120 KPa, as given in Figure 4, respectively. The addition of the virgin coconut oil and cooking coconut oil can decrease the tensile strength of PHBV by 50% (Figure 5) and the tensile modulus by 6-7% (Figure 6). The addition of the coconut oil to the 2% w/v PHBV-Latex matrix results in a 10% increase in tensile modulus compared to the 3% w/v PHBV-Latex matrix, especially for cooking coconut oil (CC) of 2P12-L8-CC1 (Figure 5b). However, there are very important variations in the tensile elastic modulus and yield strength for the 2% w/v PHBV-Latex-Virgin coconut oil (2Px-Lx-VC1). The reason is that the virgin coconut oil has an extra 55% saturated fat, but the cooking coconut oil has nil. According to Figure 2-3, the degree of crystallinity is increase in 3Px-Lx-C1, however, its melting temperature presents lower than 2Px-Lx-C1. The effect of low melting temperature obviously

influences to the reduction in modulus and yield strength of both 3Px-Lx-VC1 and 3Px-Lx-CC1 composites. The presents of the coconut oil in the blends are attributed to conformity declaration of plastic deformation after yield until break, particularly the cooking coconut oil. Without the coconut oil, this property is not dominated. Increase the amount of coconut oil twice to the PHBV-Latex matrix affects the short elongation at break of this composite and also quickly 50% failures.

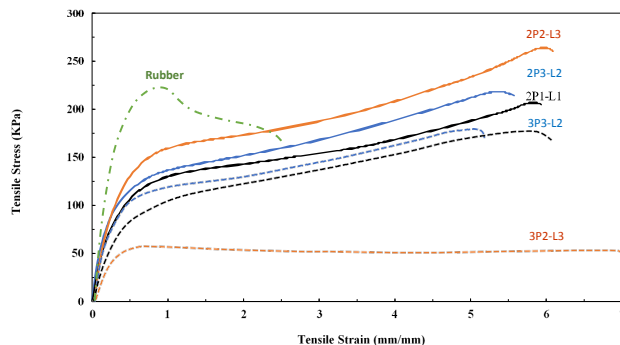


Figure 4: Tensile stress as a function of tensile strain of PHBV (P) and latex (L) in two PHBV concentrations (2% and 3% w/v of PHBV: 2P, 3P), with the blend composition ratio of 3:2, 1:1, and 2:3; for example, 2P2-L3 represents 2% (w/v) of PHBV with the addition of latex in the ratio of 2:3; compared to rubber

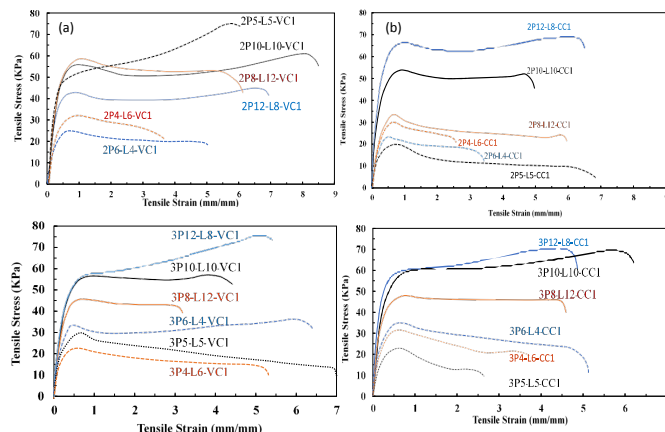


Figure 5: Tensile stress as a function of tensile strain of P/L samples in two PHBV concentrations (2% and 3% w/v of PHBV-2P, 3P) with the addition of virgin coconut oil (VC) and cooking coconut oil (CC) to the P/L components by two composition series in the ratio of (I) 12:8:1 10:10:1, 8:12:1, and (II) 6:4:1, 5:5:1, 4:6:1 (a) 2Px-Lx-VC1, (b) 2Px-Lx-CC1, (c) 3Px-Lx-VC1, and (d) 3Px-Lx-CC1

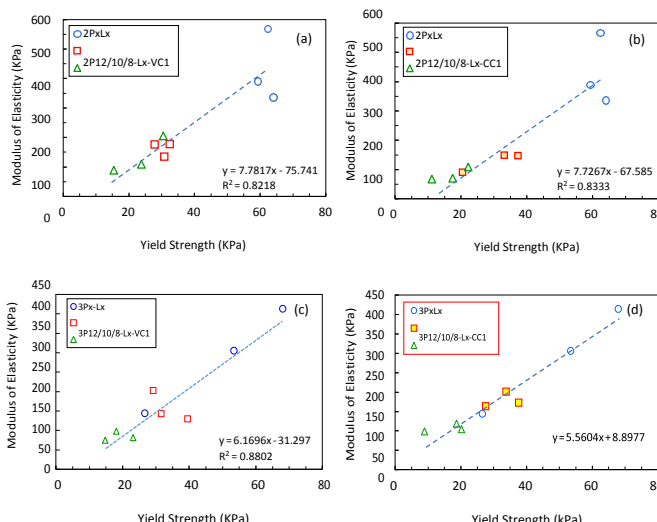


Figure 6: Modulus of elasticity related to yield strength of PHBV/Latex/Vegetable oil in two PHBV concentrations (2% and 3% w/v of PHBV-2P, 3P) with the addition of virgin coconut oil (VC) and cooking coconut oil (CC) to the P/L components which are compared to 3 groups of mix- and unmix vegetable coconut oils (a) 2% PHBV-Latex-Virgin coconut oil, (b) 2% PHBV-Latex-Cooking coconut oil, (c) 3% PHBV-Latex-Virgin coconut oil, and (d) 3% PHBV-Latex-Cooking coconut oil

4. CONCLUSIONS

The results acquired outstandingly that adding the coconut oil in PHBV and natural latex mixtures can develop the physical characterizations of the PHBV-Latex blends, specifically their thermal and mechanical properties. The degree of crystallinity is inversely proportional to the melting temperature for 3Px-Lx-C1 which is lower than 2Px-Lx-C1. The 3% w/v of PHBV-Latex-Coconut oil blends presents higher melting temperature than the 2% w/v of PHBV-Latex-Coconut oil mixtures. Adding coconut oil mixes show a lower melting temperature (166-167⁰C) compared to the mixture without coconut oil (168-169⁰C). The virgin coconut oil mixes specify poor inconsistency of the melting temperature, enthalpy, and degree of crystallinity. Melting points of 3Px-Lx- C1 with the coconut oil obviously decrease melting temperature in the range of 1.0-1.5⁰C. No coconut oil (2Px- Lx and 3Px-Lx) shows the ultimate tensile strengths at 130-160 KPa and 60-120 KPa, respectively. The addition of the coconut oil can decrease the 50% of tensile strength and the 6-7% of tensile modulus. The cooking coconut oil added to the 2% w/v PHBV-Latex matrix causes a 10% increase in tensile modulus compared to the 3% w/v PHBV-Latex matrix. The presents of the coconut oil in the blends are qualified to correspondence of plastic deformation after yield.

5. ACKNOWLEDGEMENTS

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