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Effect of maleic anhydride compatibilizer addition on mechanical properties of polylactic acid (PLA)/cellulose acetate (CA) composites film

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ABSTRACT

Environmental problems caused by the use of undegradable conventional plastics are still the major issue. According to the Badan Pusat Statistik (BPS) in 2021, plastic waste in Indonesia accumulated as much as 66 million tons per year and is expected to raise gradually. PLA and CA, derived from renewable resources, are biodegradable, thermoplastic, resistant to pressure, and are often used as raw materials for the manufacture of composite plastics. PLA is hydrophobic and CA is hydrophilic, so a compatibilizer is needed as a substance that can improve the mechanical properties, compatibility, and homogeneity of the resulting composite film. This research aims to obtain the ratio of PLA/CA and the concentration of maleic anhydride (MA) compatibilizer to produce PLA/CA composites film with good mechanical strength and according to packaging material standards. The method in this research is solvent casting by synthesizing composite films through sample preparation, modification of CA with MA, grafting of PLA/CA and MA, synthesis of composite films of PLA/CA and MA, as well as several characteristic tests. The results showed that the obtained films were identified as having PLA, CA, and MA, had a relatively smooth surface and were degraded at a temperature treatment of 543ºC. The best film was obtained from mass variations of PLA/CA and MA (6:4:1,5 gram) with a tensile strength of 7,38 MPa, and elongation at break reached 18,11% and met the packaging standard values by Japanese Industrial Standard (JIS).

ABSTRAK

Permasalahan lingkungan yang disebabkan oleh penggunaan plastik konvensional yang sukar terdegradasi masih terus berlanjut. Menurut Badan Pusat Statistik (BPS) pada tahun 2021, limbah plastik di Indonesia mencapai 66 juta ton per tahun dan diperkirakan akan terus meningkat. PLA dan CA berasal dari sumber daya terbarukan, bersifat *biodegradable*, termoplastik, serta tahan terhadap tekanan, kerap kali dijadikan sebagai bahan baku pembuatan plastik komposit. PLA bersifat hidrofobik dan CA bersifat hidrofilik, sehingga diperlukan *compatibilizer* sebagai zat yang dapat meningkatkan sifat mekanis, kompatibilitas, dan homogenitas komposit *film* yang dihasilkan. Penelitian ini bertujuan untuk mendapatkan rasio PLA/CA dan konsentrasi *compatibilizer* maleat anhidrida (MA) untuk menghasilkan komposit *film* PLA/CA dengan kekuatan mekanis yang baik dan sesuai dengan standar bahan pengemas. Metode pada penelitian ini adalah *solvent casting* dengan dengan tahapan modifikasi CA dengan MA, *grafting* PLA/CA dan MA, sintesis komposit *film* PLA/CA dan MA, serta beberapa pengujian dan analisis. Hasil penelitian menunjukkan bahwa *film* yang diperoleh teridentifikasi terdapat PLA, CA, dan MA, memiliki permukaan yang relatif halus serta terdegradasi pada perlakuan temperatur 543ºC. *Film* terbaik diperoleh untuk variasi PLA/CA dan MA sebesar (6:4:1,5) gram dengan *tensile strength* sebesar 7,38 MPa, serta *elongation at break* mencapai 18,11% dan telah memenuhi standar pengemas.

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1. Introduction

Conventional plastic derived from petroleum, still has its own charm for people in the world because of its properties such as; light weight, water resistance, strength, anti-corrosion, and low price. Data submitted by the Central Statistics Agency (Biro Pusat Statistik) in 2021, showed that plastic waste in Indonesia has reached 66 million tons per year. The high number of plastics used has a negative impact on environmental sustainability, due to the nature of plastic that is difficult to decompose in the soil, thus causing the accumulation of plastic waste that pollutes the environment. Efforts has to be made to reduce these problems by altering conventional plastics with biodegradable natural raw materials or better known as bioplastics.

A polymer that has the potential to be used as a bioplastic is polylactic acid (PLA) because it is biodegradable, biocompatible, non-toxic, and easy to process [1]. PLA is a polymer derived from renewable resources because the lactic acid can be obtained from cellulose, glycerin, starch, sugar, and biodiesel residue, which has biocompatible and biodegradable properties [2][3]. The weaknesses of PLA as a packaging material are fragile and brittle. Therefore, as an efforts to increase its potential as a commercial packaging material, it is necessary to modify its mechanical strength and elasticity, by combining PLA with fillers to form a composite films [4]. One of the fillers that can be used to mix with PLA is cellulose acetate (CA).

Cellulose acetate (CA), used as reinforcement to improve the physical and mechanical properties of PLA, is a very promising reinforcement filler to be developed because it has high crystallinity and tensile strength [5]. The main challenge in the synthesis of PLA/CA composites film is the differences in the properties of PLA and CA. The mixture of PLA (hydrophobic) and CA (hydrophilic) can cause unstable surface tension and make the mixture homogeneity difficult to achieve. The homogeneity of the mixture can be improved by the addition of a compatibilizer agent. A compatibilizer is a specific compound that can be used to combine incompatible polymers into a stable mixture through intramolecular bonds.

Research conducted by Gunawardene et al [6] showed that using maleic anhydride (MA) as a compatibilizer in the manufacture of PLA/starch composites film can increase elongation at break up to 150%. The advantages of using MA as a compatibilizer are easy mixing with polymers, low price, and low toxicity [7]. Based on the description above, it is necessary to conduct research on the effect of CA filler and MA compatibilizer addition to the PLA matrix on the mechanical strength and homogeneity of PLA/CA composites film as packaging materials. The results of this research are expected to be an alternative solution in reducing the use of conventional plastics derived from petroleum. The aim of this study was to obtain the optimum concentration of maleic anhydride (MA) as a compatibilizer to produce PLA/CA composites film with good mechanical strength and according to packaging material standards.

2. Materials and Methods

2. 1 Materials

The materials used in this research, including distilled water, acetone, cellulose acetate (CA), chloroform, maleic anhydride (MA), polyethylene glycol (PEG), and polylactic acid (PLA), were obtained from Merck, Indonesia.

2. 2 Synthesis of PLA/CA Composite Film modified by MA

CA powder (5; 4; 3; 2 grams) was dispersed in acetone with a ratio of (1:10) w/v and stirred using a magnetic stirrer at a constant speed. Plasticizer polyethylene glycol (PEG) as much as 10% w/w of CA solution, was put into a suspension that had previously been added with MA (0.5; 1; 1.5; and 2 grams) and stirred for 60 minutes using magnetic stirrer. The viscous solution formed is CA modified by MA. PLA as much as 5; 6; 7; and 8 grams dissolved in chloroform in a ratio (1:5) w/v. The PLA solution was dispersed using a magnetic stirrer to obtain the dispersed phase. The homogeneous CA modified by MA solution was added dropwise into the PLA solution while stirring using a hot plate with the help of a magnetic stirrer, rotating speed of 5,000 rpm, at room temperature for 3 hours [8]. The MA-modified PLA/CA suspension was then irradiated using ultrasonic waves for 60 minutes. The composite film was obtained, known as solvent casting method, by pouring MA-modified PLA/CA suspension into a glass plate, size 20 x 20 cm, and a petri dish to form a film with a thickness of 0.5 mm [9]. The film formed was then dried at room temperature for ± 24 hours to evaporate the chloroform and acetone. The dry MA-modified PLA/CA composite film was removed from the glass plate and petri dish for further characteristic tests.

2. 3 Composite Film Testing and Analysis

The testing and analysis of the MA-modified PLA/CA composite film was carried out with several tests, i.e. mechanical test (tensile strength and elongation at break), the Fourier Transform Infra Red (FTIR) functional group test, Scanning Electron Microscope (SEM) morphology test, and Differential Scanning Calorimetry-Thermogravimetric Analysis (DSC-TGA) test.

2. 3. 1 Analysis of Tensile Strength and Elongation at Break

Tensile strength and Elongation at break are used for mechanical strength analysis and provide information on thermo-mechanical properties of film composites using a 10 kN Universal Testing Machine (UTM).

2. 3. 2 Fourier Transform Infra-Red (FTIR) Analysis

Fourier Transform Infra-Red (FTIR) spectrophotometry was used for the analysis of functional groups contained in the composite film in the wavelength range of 500-4000 cm-1 using Thermo Scientific type Nicolet iS5.

2. 3. 3 Scanning Electron Microscope (SEM) Analysis

Scanning Electron Microscope (SEM) was used for morphological and topological analysis of composite films with 100X magnification using JEOL JSM-6510LA.

2. 3. 4 Differential Scanning Calorimetry-Thermogravimetric Analysis (DSC-TGA)

Differential Scanning Calorimetry-Thermogravimetric Analysis (DSC-TGA) was used to analyze the amount of energy and degradation ability of composite films in the temperature range 27-543ºC using Perkin Elmer Jade DSC.

3. Results and Discussion

3.1 Analysis of Tensile Strength and Elongation at Break

This research was carried out with several variations of the compatibilizer addition, from 0.5 grams to 2 grams, and resulted in an increase in mechanical properties in the form of tensile strength and elongation at break up compared to PLA only film. The addition of a compatibilizer improved the compatibility between PLA and CA as well as homogenizing two different properties, the hydrophobic PLA and hydrophilic CA. However, the addition of 2 grams of an MA compatibilizer showed a decrease in the resulting tensile strength and elongation at break values. This happens because the bond energy of the composite film decreases. The addition of a compatibilizer does not always show an increase in the mechanical properties of the obtained composite film, because the larger the molecule resulted from the modification of PLA-CA-MA the weaker bond energy, so that it will reduce the tensile strength of the resulting composite film [10]. The best synthesis of PLA/CA composites film in this study was the addition of 1.5 grams of maleic anhydride. The same result was also reported by Akil, Park, and Petersson [11]–[13]. The PLA/CA composite film in this study complied with the Japanese International Standard (JIS) with several standards, i.e. the minimum tensile strength value of 0.392 MPa, elongation at break 10%, and thickness 0.25 mm [14]. The results of the mechanical test can be observed in Table 1.

Table 1. The results of the mechanical test of MA-modified PLA/CA composite film

Sample	***Thickness* (mm)**	***Width* (mm)**	***Gauge Length* (mm)**	***Tensile strength* (MPa)**	***Elongation at break* (%)**
	***Japanese International Standard* (JIS)**				
	<0.25 mm	**-**	**-**	**≥0.392 MPa**	**≥10%**
PLA	0.06	5.00	30.00	4.52	16.30
PLA/CA/MA 6:4:0.5	0.16	20.66	49.22	6.65	14.75
PLA/CA/MA 6:4:1.0	0.21	19.62	49.17	6.31	15.45
PLA/CA/MA 6:4:1.5	0.18	19.97	49.12	7.38	18.11
PLA/CA/MA 6:4:2.0	0.24	20.31	50.39	5.44	13.00

3.2 Fourier Transform Infra-Red Analysis Results

The composite film was tested by Fourier Transform Infra-Red (FTIR) which aims to determine the presence of functional groups formed from the resulting mixture. The FTIR analysis results of the MA-modified PLA/CA composite film are shown in Figure 1.

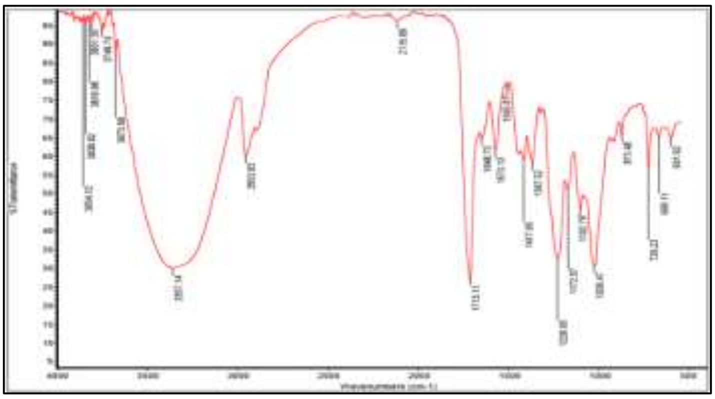

Figure 1. FTIR Test Results of MA-modified PLA/CA Composite Film (6:4:1,5)

The results of the FTIR test for the best composite film with variations of MA-modified PLA/CA with a ratio of (6:4:1.5) gram showed the presence of functional groups such as –OH, C=O, C-O-C, C-O, C-H, and -COOH, with deformation at the peaks in the specific wavelength formed as shown in Table 2. The appearance of the specific peak of functional groups indicate that PLA, CA, and MA have been perfectly composited [15]–[17].

Table 2. Comparison of Literature FTIR Test with Research Results

Functional group	**wavenumbers (cm^{-1}) (Souhoka, 2018; Maharana, 2015; Batori, 2018)**	**wavenumbers (cm^{-1}) (This research)**
-OH	3510-3648	3357.14
C=O	1735-1770	1713.11
C-O-C	1230-1250	1228.65
C-O	1000-1300	1026.47
C-H	600-3000	1417.65
-COOH *deformation*	500-1000	669.11

3.3 Scanning Electron Microscope (SEM) Analysis Results

The SEM test results showed that the addition of the MA compatibilizer improved the properties of PLA and CA. This can be observed from the surface of the film which is relatively smoother and hollowless compared to samples made of only PLA and CA. This statement is supported by research conducted by Castiqliana et al [18], where the addition of MA as a compatibilizer shows a good distribution on the matrix and will adhere to the filler to form a strong interface. Thus, it can also be concluded that the addition of a maleic anhydride compatibilizer can increase the compatibility and homogeneity of the composite film. The comparison of the SEM test results of the composite film produced is shown in Figure 2.

a b

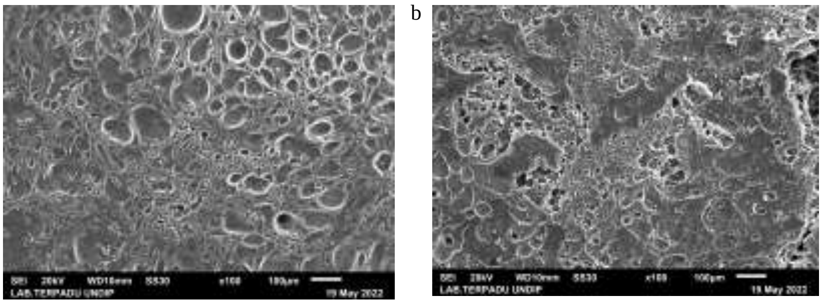

Figure 2. SEM test results on composite films; (a) PLA/CA and (b) MA-modified PLA/CA

3.4 Results of Differential Scanning Calorimetry-Thermogravimetric Analysis (DSC-TGA)

Thermal analysis was carried out to determine the amount of energy and the degradation ability of the resulting composite film as a function of temperature. The results of the Differential Scanning Calorimetry-Thermogravimetric Analysis (DSC-TGA) analysis are shown in Figure 3.

a. b.

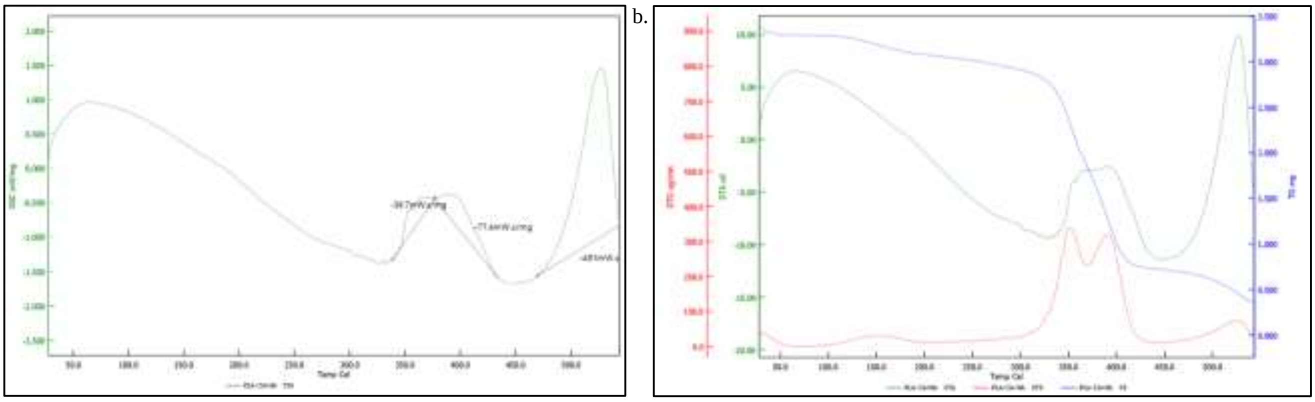

Figure 3. (a) DSC test results; (b) TGA test results

Figure 3 (a) shows a graph for measuring the properties of a 3.40 mg composite film based on the energy released. In the figure it can be seen that there are three main peaks formed, at 375ºC, 430ºC, and 543ºC with the energy released of 39681.51 µW.s/mg; 77446.71 µW.s /mg; and 460944.58 µW.s /mg respectively. According to Muharrami (2014), the temperature at the peak identifies the initial melting point to the end of the composite film, while the enthalpy indicates the energy required to melt the film. Figure 3 (b) shows the size of the composite film which was degraded by treatment with a temperature from 0ºC until 543ºC. The final mass obtained after being treated with the heat for 52 minutes that the composite film with an initial mass of 3.40 mg or 3400 µg is 356.63 µg. These results indicate a good and very fast degradation ability of the composite film. Based on these results, the PLA/CA/MA composite film has the potential to become a packaging material to replace conventional plastics which are difficult to degrade [19], [20].

4. Conclusion

The addition of CA to the PLA matrix for the synthesis of PLA/CA composites film with ratios (5:5), (6:4), (7:3), and (8:2) can increase the mechanical strength with the best results obtained in the form of tensile strength, 7.38 Mpa, and elongation at break, 18.11%. The concentration of the maleic anhydride compatibilizer which produces PLA/CA composites film with a good level of homogeneity is obtained in the addition of 1.5 grams with a ratio of PLA/CA (6:4) grams.

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