Utilization of Biodiesel By-Product Glycerol as Plasticizer for Bioplastic Print Lamination

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Abstract. Glycerol as a by-product of biodiesel continues to increase in Indonesia. Glycerol has a vast potential implementation in the cosmetic, pharmaceutical, and printing industries. This research aims to utilize glycerol as a by-product of palm biodiesel as a plasticizer in bioplastic applications as an alternative material for print laminating. Transesterification is carried out to separate crude glycerol from fatty acid methyl ester (biodiesel). Purification of crude glycerol was carried out using phosphoric acid. The results showed that the purified glycerol obtained from the by-product of biodiesel production could be used as a plasticizer for printed lamination bioplastic application. The purified glycerol's pH, density, and viscosity were 7.27; 1,248 g/mL; and 35.63 CST, respectively. The trial of printed lamination has proven that bioplastic lamination is lighter than conventional laminating, according to the higher CIE L* value. Moreover, the total color difference of prints laminated by bioplastics is lower than prints with conventional laminating, indicated by the value of delta E in all color samples of bioplastic laminated prints, which are lower than conventional laminating.

Keywords: glycerol, biodiesel, bioplastic, print laminating.

1 Introduction

Biodiesel can be synthesized from vegetable oils, especially palm oil and methanol, through a transesterification reaction using an alkaline catalyst. This reaction produces fatty acid methyl ester (biodiesel) and crude glycerol (crude glycerol) as by-products. One kilogram of crude glycerol is produced in producing nine kilograms of biodiesel [1]. This number continues to increase in line with the increase in biodiesel production in Indonesia. The mandatory biodiesel policy supports the increase in biodiesel production in Indonesia through the Minister of Energy and Mineral Resources No. 20 of 2014, which regulates the mandatory minimum use of biodiesel as a fuel mixture in stages until 2025 by 30% [2].

Crude glycerol produced from transesterification generally has low purity because it still has residues or impurities, which vary according to the conversion method, the type of alcohol, and the catalyst used. The resulting glycerol has low commercial value. Therefore, purification is necessary to obtain high-value glycerol [1].

Glycerol is a chemical product known commercially as glycerin, which is colorless, odorless, and viscous. According to IUPAC, glycerol is classified as alcohol under the name 1,2,3-propanetriol, with soluble in all ratios with water and hygroscopic properties derived from the three hydroxyl groups. This term refers to commercial glycerin products with a purity above

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95% [3]. The various applications of glycerin are broad, such as in the pharmaceutical, cosmetic, food, and polymer fields. In the case of polymers, glycerol functions as a plasticizer for the manufacture of bioplastics [4].

The plasticizer is an organic material that can increase polymer flexibility and reduce stiffness. However, adding excess plasticizer can reduce the molecular mobility of the interaction between starch and plasticizer (Kamsiati, Herawati, and Purwani, 2017). The function of glycerol is to absorb water as a crystallizing agent and plasticizer. The plasticizer is a compound that can increase the flexibility, strength, and distortion of the biopolymer matrix by reducing the electrostatic charge and, at the same time, increasing the flexibility, crack resistance, and dielectric constant [5].

Lamination is coating the print substrate with a thin plastic material to protect the print from damage, friction, and other factors that cause the print to fade. Especially on paper printing media that are hygroscopic, the lamination process can protect the printout from damage caused by water, moisture, and light. Lamination with the plastic film is an option to overcome this problem, making the prints have good strength and temperature resistance and are transparent [6]. Therefore, this research aims to utilize glycerol as a by-product of palm biodiesel as a plasticizer in bioplastic applications as an alternative material for laminated prints.

2 Research Methods

2.1 Palm oil transesterification

Base catalyst (KOH) 1% mixed with methanol as much as 15% of the palm oil mass. Refined Bleached Deodorized Palm Oil (RBDPO) was heated in a three-neck flask equipped with a condenser, thermometer, and magnetic stirrer, followed by the addition of methanol and catalyst at a temperature of 55-60 ºC and stirring at a constant speed. The transesterification reaction takes between 45-75 minutes. Separation of biodiesel and crude glycerol was carried out in a separating funnel. Two layers will form after letting it sit for at least 8 hours. The bottom layer is crude glycerol and the top layer is biodiesel.

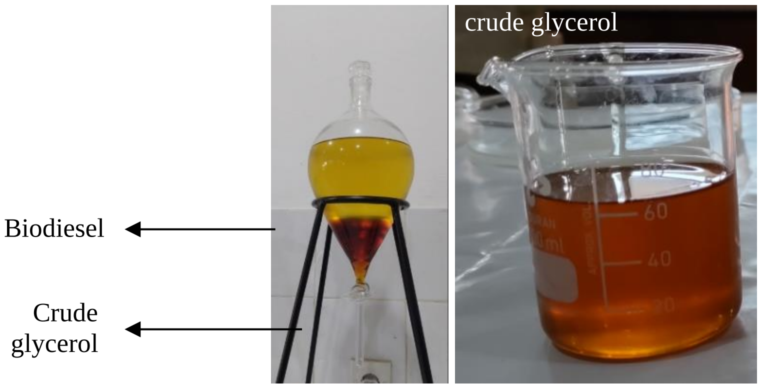

Fig. 1. Separation of biodiesel and crude glycerol and

2.2 Glycerol purification

The crude glycerol was put into a glass beaker and heated using a hotplate to a temperature of 60ºC. Phosphoric acid (H_3PO_4) 6% was added gradually in a ratio of 3:10. It was Stirred continuously using a magnetic stirrer until it reached a temperature of 85-90ºC for 30 minutes. Then left for 24 hours [7], [8]. Then, the glycerol was filtered to take the filtrate and discard the filtered salt [8].

2.3 Bioplastics synthesis as printed lamination materials

Bioplastics are made by dissolving 5 g of sago starch in 95 ml of distilled water. A total of 2 mL of glacial acetic acid was added while stirring. Furthermore, 2 mL purified glycerol were added, then heated on a hotplate stirrer at a temperature of 60˚C until gelatinization occurred. The liquid bioplastic is then poured into a mold and dried for 24 hours at room temperature. The implementation of bioplastic as a lamination material on the printed results is carried out by using a laminating tool with samples produced.

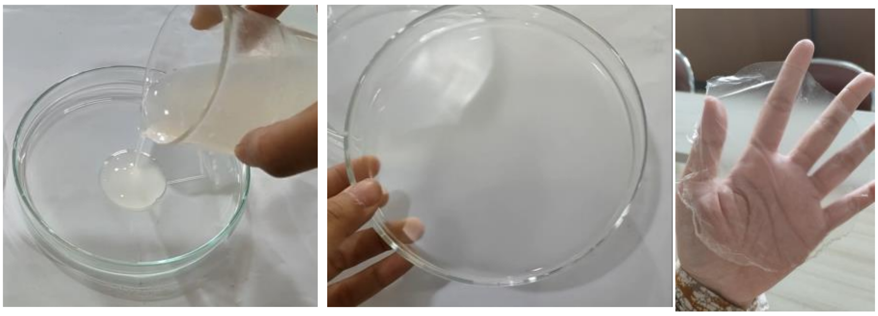

Fig. 2. Bioplastics produced with glycerol as a plasticizer

2.4 Samples characterization

Analysis of physicochemical properties carried out on crude glycerol, purified glycerol, and commercial glycerol included testing for density, viscosity, and pH. The tests on the resulting bioplastics were thickness, grammage, opacity, brightness, light scattering coefficient, and light absorption coefficient. The effect of laminated prints using bioplastic compared to commercial laminating was carried out by measuring the color of the printout CIE L*a*b* using a Spectrodensitometer.

3 Result and Discussion

The glycerin produced in this study can be seen in Figure 3 below. The results of the analysis of the physical properties of crude glycerol, purified glycerol, and commercial glycerin are listed in Table 1. Crude glycerol was purified using phosphoric acid, with a yield of 38.87%.

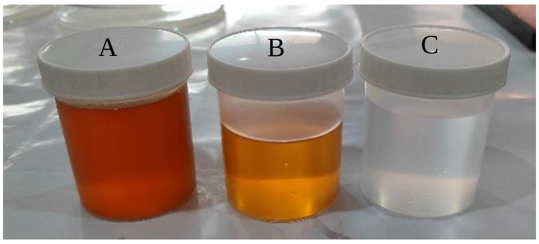

Fig. 3. (A) crude glycerol; (B) purified glycerol; and (C) commercial glycerin

Table 1. Glycerol characteristics

Samples	pH	Density (g/mL)	Viscosity (cSt)
Crude glycerol	9.95	1.094	980.00
Purified glycerol	7.27	1.248	35.63
Commercial glycerol	6.06	1.159	29.03

The pH value of crude glycerol is 9.97, which means that glycerol is alkaline because, in crude glycerol biodiesel by-products, there are still alkaline catalyst residues remaining from the transesterification reaction. While the glycerol test results have a relatively neutral pH of 7 because it has gone through a phosphoric acid-based acidification process. While commercial glycerin generally has a neutral pH, which is in the range of 6-7 [4].

The density of purified glycerol is 1.248 g/mL, higher than conventional glycerol, which is 1.159 g/mL. However, the density of purified glycerol is closer to the density of standard glycerol BS 2621: 1979, which is 1.2671 g/mL [9]–[11]. Furthermore, purified glycerol has a much lower viscosity than crude glycerol.

The results of testing for bioplastics using glycerol as a plasticizer, compared to commercial laminating materials, are shown in Table 2. The resulting bioplastic has a lower grammage and thickness than conventional laminating materials, with the brightness and opacity of bioplastics. However, the thickness of the bioplastic is 40.33 microns, in line with previous similar research, the biodegradable film as a laminating mulberry paper of 40 microns [6].

Table 2. Bioplastic and commercial laminating characteristics

Samples	Grammage (g/m^2)	Thickness (micron)	Brightness (%)	Opacity (%)	Light Scattering Coefficient	Light Absorpsion Coefficient
Bioplastics	47.11	40.33	36.35	10.40	0.59	0.14
Commercial laminating	105.34	87.17	53.91	14.55	1.02	0.13

Bioplastic lamination was implemented on printed products using a laminator, shown in Figure 4. The CIE L*a*b* and color difference between the printed product without lamination and the laminate are shown in Table 3.

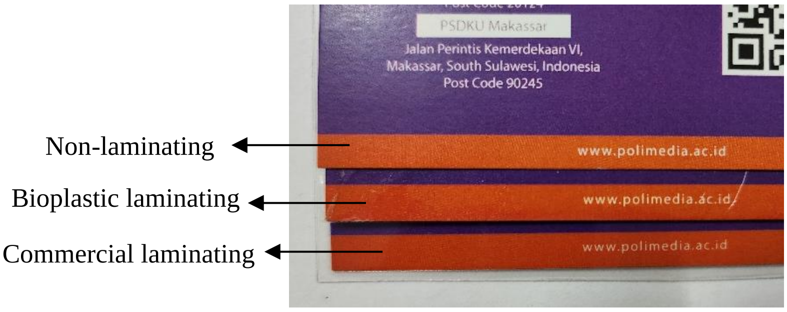

Fig. 4. Non laminating and laminate printed products

Table 3. CIE L*a*b* measurements of printed product

Print Color	Samples	CIE L*	CIE a*	CIE b*	Delta E
Violet	Non-laminating	31.11	30.01	-32.49	
	Commercial laminating	27.98	30.35	-34.32	3.64
	Bioplastic laminating	28.56	28.65	-33.72	3.14
Orange	Non-laminating	53.96	44.67	49.15	
	Commercial laminating	49.18	49.03	48.49	6.50
	Bioplastic laminating	50.76	48.99	49.46	5.39
White	Non-laminating	90.73	0.4	-7.65	
	Commercial laminating	86.9	0.13	-7.25	3.86
	Bioplastic laminating	88.72	0.65	-6.48	2.34

Adding lamination to the printed products reduces the lightness of the colors shown in the CIE L* values in Table 3. Bioplastic laminates are brighter than conventional laminates.

4. Conclusion

Based on the results of this research, the purified glycerol obtained from the by-product of biodiesel production can be used as a plasticizer in the application of printed lamination. Bioplastic prototypes using glycerol as a plasticizer have been produced and used as laminates for printed products. The trial of printed lamination has proven that bioplastic lamination is lighter than conventional laminating, according to the higher CIE L* value. Moreover, the total color difference of prints laminated by bioplastics is lower than prints with conventional laminating, indicated by the value of delta E in all color samples of bioplastic laminated prints, which are lower than conventional laminating.

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References

[1] R. Purwadi, M. T. A. P. Kresnowati, L. Badriyah, A. A. D. Puri, and R. Aisyah: Pemanfaatan gliserol sebagai limbah biodiesel melalui proses biologik 1: Pemilihan mikroba, *J. Tek. Kim. Indones.*, vol. 12, no. 1, p. 213 (2018), doi: 10.5614/jtki.2013.12.1.6.

[2] M. Agustina, R. Findriyani, S. Tiara, S. Mulya, and N. A. Sasongko: Potential of Glycerol and Derivatives Based on Palm Oil as a Green Solvent Palm oil Transesterification reaction, pp. 22–27 (2020).

[3] F. D. Pitt, A. M. Domingos, and A. A. C. Barros: Purification of residual glycerol recovered from biodiesel production," *South African J. Chem. Eng.*, vol. 29, no. October 2018, pp. 42–51 (2019) doi: 10.1016/j.sajce.2019.06.001.

[4] Azaria Robiana, M. Yashin Nahar, and Hamidah Harahap: Pemanfaatan Gliserin Dari Residu Gliserin Sebagai Plasticizer Untuk Pembuatan Bioplastik Dengan Bahan Baku Pati Bonggol Pisang Kepok, *J. Tek. Kim. USU*, vol. 5, no. 4, pp. 26–32 (2017), doi: 10.32734/jtk.v5i4.1551.

[5] I. Inayati, A. Abdulloh, and Z. Bagus R: Fabrication of Bioplastic from Rice Straw, *Equilib. J. Chem. Eng.*, vol. 4, no. 1, p. 17 (2021) doi: 10.20961/equilibrium.v4i1.43155.

[6] A. Memon, S. Ithisoponakul, S. Pramoonmak, M. Lawsuriyonta, D. Leenoi, and N. Passadee: A development of laminating mulberry paper by biodegradable films, *Energy Procedia*, vol. 9, pp. 598–604 (2011) doi: 10.1016/j.egypro.2011.09.070.

[7] Johnson: Pemurnian gliserol dari hasil samping pembuatan biodiesel dengan penambahan asam anorganik, University of North Sumatra (2021).

[8] P. Pardi: Pemurnian Gliserol Kasar Dari Residu Gliserol Hasil Samping Pembuatan Biodiesel, *J. Sains dan Teknol. Reaksi*, vol. 4, no. 2, pp. 13–17 (2016) doi: 10.30811/jstr.v4i2.35.

[9] S. Nadeak, J. Mentari Hasibuan, L. Widya Naibaho, and M. Suriani Sinaga: Pemanfaatan Limbah Cangkang Telur Ayam Sebagai Adsorben Pada Pemurnian Gliserol Dengan Metode Asidifikasi Dan Adsorpsi, *J. Tek. Kim. USU*, vol. 8, no. 1, pp. 25–31 (2019) doi: 10.32734/jtk.v8i1.1872.

[10] M. S. Sinaga, M. R. Ramadhan, G. Rico, and W. G. T. Sitompul: Effect of Acidification Mole Ratio and Solvent Volume Ratio of Glycerol Purification, *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 505, no. 1 (2019) doi: 10.1088/1757-899X/505/1/012116.

[11] M. S. Ardi, M. K. Aroua, and N. A. Hashim: Progress, prospect and challenges in glycerol purification process: A review, *Renew. Sustain. Energy Rev.*, vol. 42, pp. 1164–1173 (2015) doi: 10.1016/j.rser.2014.10.091.