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Development of Green Composite Based on Recycled-Low Density Polyethylene (r-LDPE) as an Environmentally Friendly Packaging

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Abstract: Low-Density Polyethylene (LDPE) is one of the most popular and commonly used petroleum-derived thermoplastics for packaging. The large production of LDPE has an environmental impact. Reducing production can be done by recycling LDPE (r-LDPE) and adding organic fibres as a filler that is easily decomposed. Cattle farming solid waste as a fibre source was mixed with r-LDPE with coupling agent maleic anhydride (MA). Before use, the cow manure was processed through a bleaching and hemicellulose removal process, which resulted in Cow Manure Fiber (CMF). The CMF was analyzed using FTIR spectroscopy and microscopic fibre dimension analysis. The FTIR results showed peaks at wavenumbers 3538 and 1056 cm^{-1}, representing the -OH, -C-O and -CH functional groups from the cellulose structure. The resulting composites were tested for physical properties, including elastic modulus, yield stress, and elongation. Pure LDPE material was also used for comparison. The best physical properties of the composites were obtained by composites with 95% r-LDPE, 5% CMF, and 2% MA.

Keywords: Cellulose; Cow Manure Fibre (CMF); Green Composite; Maleic Anhydride (MA); Recycled-Low-Density Polyethene (r-LDPE).

Introduction

Low-density polyethene (LDPE) is a petroleum hydrocarbon-derived thermoplastic containing ethylene monomers [1]. LDPE is widely used as packaging due to its high chemical resistance [2]. Every year, 9 million tons of LDPE products are produced [3]. The mass production of LDPE results in environmental problems, needing 500-1000 years to decompose [4]. Reducing LDPE production can be done by reusing and recycling the materials. Recycled LDPE (r-LDPE) waste can be reused by making various modifications.

Recycled low-density polyethene is modified to produce an excellent composite physical and chemical performance. Modification can be done by adding inorganic and organic materials such as natural fibres as fillers. The inorganic materials that are widely used as fillers include diatomite [5], zeolite [6], and clay [7]. Some natural fibres that can be used include pineapple fibre [8], bamboo [9], and wood fibre [5]. Shih et al., 2021 [5] conducted the addition of 57% wood fibre into r-LDPE, increasing the hardness value of the material to 70 ShD. Compared to commercial LDPE of 50-60 ShD. In addition, using 47% wood fibre and 2.37% maleic anhydride increased the elongation of r-LDPE by 38.38%. However, applying wood and other natural fibres still has to compete with the furniture industry. Therefore, finding alternative fibres that are accessible, cheap, and abundant is urgently needed.

One of the potential wastes used as a substitute material for natural fibres, with high cellulose content, is cow manure (CM). CM waste has a cellulose content of up to 32.40% [10], so it can potentially be a filler for the reinforcement of environmentally friendly composite. In addition, adding natural materials to thermoplastics will increase the rate of plastic decomposition and reduce excessive plastic production [11]. However, the lower compatibility of organic fibres and r-LDPE matrix resulted in decreased composite performance, such as tensile strength, elastic modulus, yield stress and elongation. Increasing the adhesion and compatibility between the r-LDPE and organic fibres by applying the coupling agents/compatibilizers [5]. One of the coupling agents that can be used is maleic anhydride (MA) [12]. This material provides a better adhesion force to the mixture of natural fibres with LDPE [5].

Research Methods

Drying of Cow Manure

Cow manure is air-dried for approximately one week to remove gas and odour.

Isolation of Cellulose from Cow Manure Solid Waste

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Bleaching Process

100 g of cattle farm solid waste was soaked in 3%wt sodium chlorite ($NaClO_2$) or HCl or H_2O_2 solution at acidic pH for 3 hours at 80 ºC. The mixture was kept at room temperature for 24 hours. The sample was washed with distilled water until neutral. This bleaching process was repeated twice [13].

Hemicellulose removal

After bleaching, the samples were soaked in a water bath with 4%wt NaOH for four h at 60 oC. The samples were filtered with a vacuum pump and dried, resulting in CMF. The CMF was used for the next stage. The samples were tested with an optical microscope to determine the dimensions of the fibres, including cell wall thickness, fibre length, and diameter, and functional group analysis was performed with FTIR [14].

Preparation of recycled LDPE (r-LDPE) from waste of packaging material

The waste of packaging materials was washed thoroughly and then dried. The waste was solidified by heating at 160 ºC until it melted and moulded into plastic ore. This plastic ore is then referred to as r-LDPE or recycled Low-Density Polyethene.

Preparation of r-LDPE composites with CMF

The r-LDPE and LDPE materials were placed in a stirring machine at 160 ºC until the material melted, then mixed with CMF and MA, and then stirred for 10 minutes at 50 rpm. After the mixing process, the material is moulded using a press machine. The plastic press was set at 170 ºC, at 50, 70 and 100 Kgf/cm^2 pressures for 5, 3 and 2 min. The composite preparation followed the composition ratio presented in Table 1.

Table 1. Composite Composition

No.	Type	CMF (wt%)	r-LDPE (wt%)	LDPE (wt%)	MA (%)
1.	A1	5	95		
2.	A2	10	90		
3.	A3	30	70		
4.	A4	50	50		
5.	B1	5		95	
6.	B2	10		90	
7.	B3	30		70	
8.	B4	50		50	
9.	C1	5	95		2
10.	C2	10	90		2
11.	C3	30	70		2
12.	C4	50	50		2
13.	D1	5		95	2
14.	D2	10		90	2
15.	D3	30		70	2
16.	D4	50		90	2

Results and Discussion

CMF Dimension Analysis

The analysis was aimed at predicting the diameter and length of the fibres. It can be seen that the varying sizes of the fibres dominated the samples. Fibre length obtained in the range of 12.4-185 µm (12.4-185 microns), and fibre diameter ranged from 2.07-41.02 µm (2.07-41.02 microns). Based on the International Association of Wood Anatomy classification, the CMF has varying fibre lengths and includes a category of short fibres (0-900 microns) [15]. Microscopic observations for CMF are shown in Figure 1.

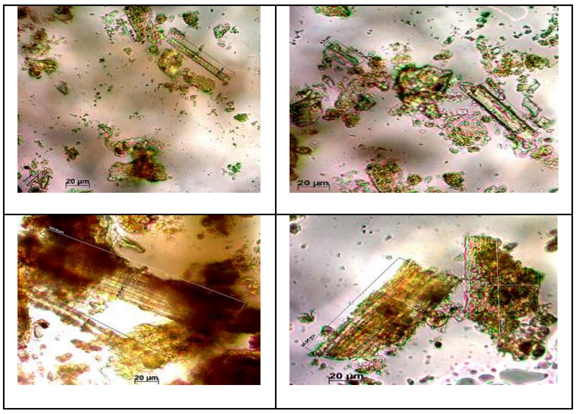

Figure 1. Dimensional analysis of CMF with magnification 100x

The presence of short fibre in CMF indicates the material has the potential to increase the strength and stiffness of the composite. In the composite performance test, the composite matrix will accept the stress and pass it on to the fibres until the maximum load is reached.

FTIR analysis

The results of FTIR analysis of CM and CMF are presented in Tables 2 and 3.

Table 2. FTIR analysis of CM and CMF

No.	Wavenumber (cm^{-1})		Assigned vibrations
	CM	CMF	
1.	3525	3538	-OH
2.	1638	1651	-C=O
3.	1024	1056	-C-O and -CH

The peak around 3525 cm^{-1} is a representation of the -OH group. The peak at 1638 cm^{-1} is assigned to the -C=O group and represents the deformation due to H_2O, which causes water absorption. Both peaks illustrate the presence of hydrogen bonds and bending hydroxyl groups in the cellulose structure in CM and CMF samples [16]. After the purification process, the wavenumbers shifted due to impurities that bound with the cellulose structure had been removed. The loss of impurities will cause more free molecular vibrations, generating considerable vibrational energy.

Physical Performance Test for Composites

Modulus Elasticity Analysis of Type A and C Composites

The results of the modulus elasticity of the composite are shown in Figure 2 and Table 3.

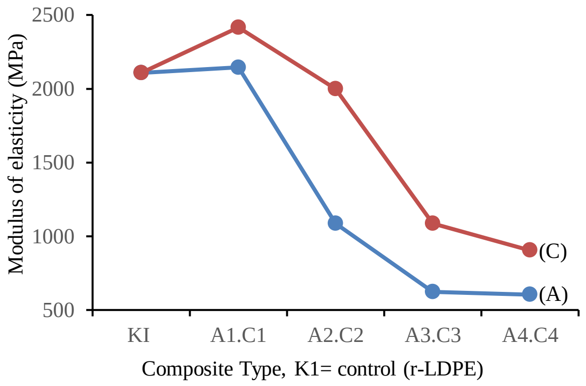

Figure 2. Modulus elasticity graphic for Type A and C composites

Table 3. The value of modulus elasticity of Type A and C composites

Type	Modulus elasticity (MPa)	Type	Modulus elasticity (MPa)
KI	2107.8		
A1	2145.0	C1	2415.5
A2	1087.0	C2	1999.8
A3	621.1	C3	1088.0
A4	603.9	C4	903.9

The elastic modulus value of type A composites decreased with the increase in CMF percentage. Adding 2% MA increased the elastic modulus value by 12% in composite C1 (5% CMF). On the other hand, increasing the filler percentage by 10-50% decreases the elastic modulus value. Adding 2% MA in a higher rate of CMF cannot increase the composite performance. The highest elastic modulus value of 2415.5 MPa was obtained by adding 5% CMF and 2% MA (Composite C1).

Yield Stress Analysis for Type A and C composite

Yield stress is the minimum stress when a material loses its elastic properties. The yield stress analysis results for composite types A and C are shown in Figure 3. The most considerable yield stress value belongs to composite type C1, with a composition of 5% CMF and 2% MA. Adding an MA coupling agent increased the yield stress value by 27.15% compared to the r-LDPE (control). The higher percentage of filler will decrease the yield stress value of the r-LDPE material.

Elongation analysis of type A and C composites

Elongation is the measurable tendency of a material to stretch when under strain until it breaks. Elongation is used to determine whether a material is ductile or brittle. A higher elongation value is observed for ductile material (strong and not easily broken). A lower value of elongation refers to brittle material [17]. Figure 4 shows the elongation values of type A and C composites. Larger elongation values are demonstrated in type C composites. Adding MA increases the compatibility between r-LDPE and CMF, thus improving the physical performance of the materials. Using 2% MA in the composites increased the elongation value by 30% in type C1 composites (Figure 4).

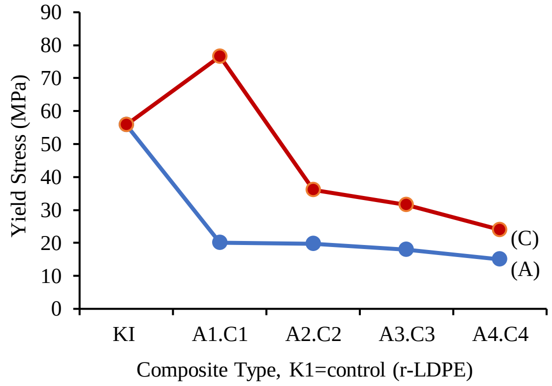

Figure 3. Yield stress analysis for type A and C composites

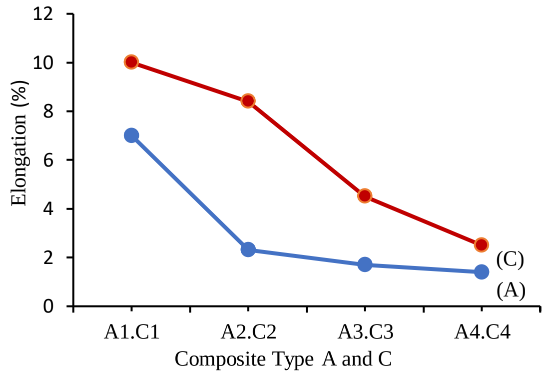

Figure 4. Elongation analysis of type A and C composites

Modulus elasticity analysis of Type B and D composites

Composites B and D are new LDPE materials, not recycled waste. Type D composites use additional MA as a coupling agent/compatibilizer. The results of the elastic modulus analysis of composites B and D are shown in Figure 5. The elastic modulus values are presented in Table 4.

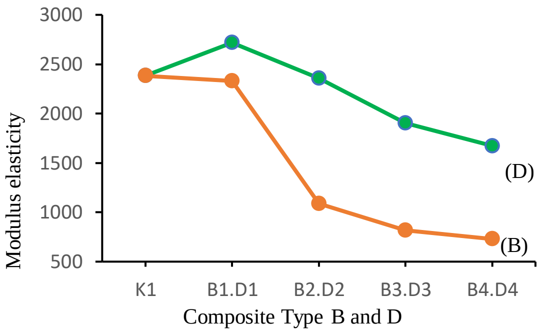

Figure 5. Modulus elasticity graphic for type B and D composite

Table 4. The value of modulus elasticity of type B and D composite

Type	Modulus elasticity (MPa)	Type	Modulus elasticity (MPa)
K1	2381.5		
B1	2328.5	D1	2717.4
B2	1087.0	D2	2358.7
B3	815.2	D3	1905.8
B4	729.2	D4	1673.5

Figure 5 shows the modulus elasticity of composite types B and D. MA as a coupling agent increases the modulus elasticity of type D composites. A total of 2% MA increased the elastic modulus by 12.4% with 5% CMF compared to pure LDPE. Increasing the CMF percentage decreased the elastic modulus value by 50% without adding MA. The reduced elastic modulus indicates greater material stiffness. Adding 2% MA increases composites' elastic modulus with 5% CMF. The more significant percentage of CMF decreases the elastic modulus value of the composite.

Y*ield stress* analysis of type B and D composite

The results of yield stress analysis of composite types B and D are shown in Figure 6. Composite type D showed a higher yield stress than composite type B. The lower yield stress value indicates that the material has lost its elastic properties and become stiffer than the control (pure LDPE), with a yield stress of 23.2 MPa. Adding CMF causes the composite to lose its elastic properties, resulting in a stiffer material. However, coupling agent MA increases in yield stress value to 48.6 MPa.

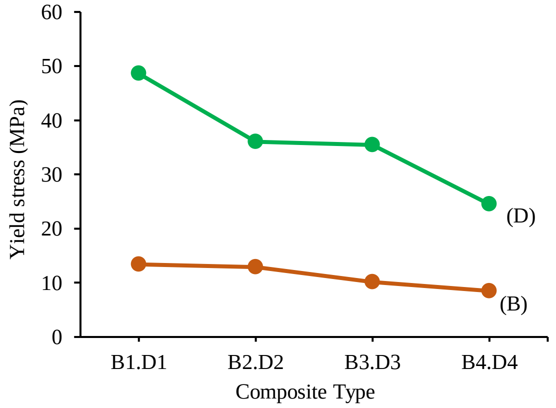

Figure 6. Yield stress analysis of composite type B and D

Elongation Analysis of Type B and D Composites

The results of elongation analysis for type B and D composites are shown in Figure 7. Based on Figure 7, the elongation value of type D composites is higher than type B. The elongation value decreases with the increase of filler percentage. Adding 2% MA with 5% CMF in composite type D1 increases the elongation value more than the B1 type. Adding MA prevents the material from breaking quickly in a tensile test. Composite type D is more malleable than B, so the D material is more suitable for packaging.

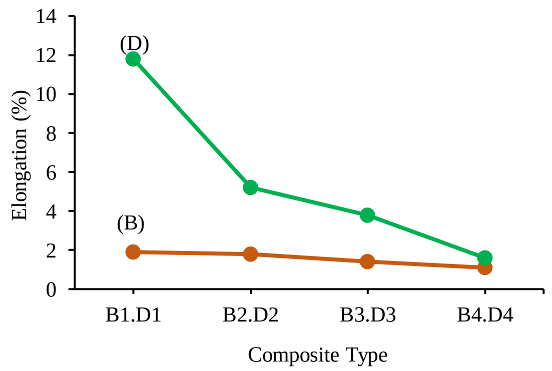

Figure 7. Elongation graphic for Type B and D composites

Conclusion

The dimensional analysis results show that CMF has the potential as a reinforcement material to increase the strength and stiffness of the composite. The best composite composition is achieved by adding 5% CMF and 2% MA, as in composite types C1 and D1. The highest elastic modulus is obtained by the D1 composite, which is 2,717.4 MPa, and the highest yield stress value is received by the C1 type composite, which is 76.6 MPa. Adding CMF and MA coupling agents to r-LDPE and LDPE material can produce packaging composites with better physical performance and are environmentally friendly.

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