Green Eggshell/Polypropylene Biocomposite

Norihan Yahya, Syuhada Mohd Tahir, Nor Habibah Mohd Rosli

Abstract: Polypropylene is a versatile polymer used in various consumer products from automotive to home appliances. Polypropylene is usually synthesized from petrochemical-based raw material which makes their waste hazardous to the environment. Eggshell, on the other hand, is highly abundant biodegradable agricultural waste that contains more than 90% calcium carbonate, a common filler used in polymer. This study investigated the effect of adding eggshell as biofiller in polypropylene matrix on its mechanical and thermal properties. The eggshell was first cleaned, heated, grinded, and sieved to 212 µm particle size. Then, the eggshell powder was mixed with propylene using mixer machine at 9:1, 7:3 and 5:5 ratio of polypropylene-to-eggshell. Finally, the composite mixtures were molded using hot press followed by cold press machine. The biocomposite samples were analyzed using Fourier transformed infrared (FTIR), thermogravimetric analysis (TGA) and tensile test. FTIR and TGA results proved the presence of calcium carbonate from the eggshell in the sample. The optimum mechanical properties obtained was for 7:3 polypropylene-to-eggshell sample with tensile strain (extension) of 0.01658 mm/mm and tensile stress of 12.714 MPa. The findings of this study showed eggshell as a feasible biofiller alternative that gives good mechanical properties complimented with major environmental advantage due to eggshell waste utilization.

***Index Terms*: Keywords: Polymer Composite, Polypropylene, Eggshell..**

I. INTRODUCTION

Polypropylene is one of the most widely used polymers due to its various applications ranging from home appliances to automotive industry. It is used widely due to its excellent thermal stability, low density value (0.90 g/cm^3), flexibility in designing and simplicity in recycling [1]. Nevertheless, the high production cost, risk hazard and awareness on the environmental issues arise from the petroleum based materials have created interest among researchers and manufacturers to find an alternative namely biocomposites that offer both low in cost and meets environmental benefit [2]-[5].

A biocomposite contains renewable resources in one of the constituents, either the matrix or the filler [4], [5]. In biocomposite, the matrix and the filler are combined to optimize their properties such as lightweight and good mechanical properties [6], [7]. The biocomposite fulfill these requirements complimented with biodegradable ability because one of the constituent comes from natural resources.

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Naturally derived mineral filler such as calcium carbonate ($CaCO_3$) is commonly used fillers in polymer composite to improve strength and stiffness [8,9]. The finest grades calcium carbonate is used primarily to modify the properties of composite whereby the lowest grades are used by means to reduce the cost [10].

Eggshell is a green filler that can be used to replace common inorganic filler due to high content of $CaCO_3$ approximately 95% and the remaining 5% are organic matters [11]-[14]. Eggshells are generated as bio-waste everyday starting from houses, food based businesses and industries, hatchery and poultry industries. The amount of the waste dumped should be considered because agricultural by-product has been listed as one of the worst environmental problems and its disposal constitutes a serious environmental hazard [15], [16]. These problems can be reduced by utilizing eggshell as an effective bio-filler in biocomposite polymer.

In this paper, chicken eggshell (ES) was used as a bio-filler in polymer matrix. Biocomposite with polypropylene (PP) as matrix and chicken eggshell as reinforcement at different mixing ratios were prepared. Thermo gravimetric analysis (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the thermal stability and structure of compounds respectively. Effect of adding eggshell as biofiller in polypropylene matrix on tensile strength was investigated.

II. METHODOLOGY

A. Materials

A commercial grade of polypropylene (PP) was used in this study without further purification. The chicken eggshells were collected from cafeteria located at UiTM Pahang, Pahang, Malaysia.

1) Experimental

The eggshells (ES) were washed, boiled in hot water for a few minutes and dried in oven at 120 °C for 20 minute to reduce its moisture content. The ES were ground to a powder using the blender and then sieved to obtain an average particle size of 212µm. PP were mixed with ES powders (10, 30 and 50 wt. %) were melt-blended in mixer machine with a screw speed of 100 rpm for 7 minutes to obtain PP/ES composites. Finally, the composite mixtures were molded using hot press followed by cold press machine.

B. Characterization

1) Fourier Transform Infrared Spectroscopy (FTIR)

The Fourier Transform Infrared Spectroscopy (FTIR) analysis were conducted on a Perkin-Elmer Spectrum 100

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FT-IR Spectrometer at room temperature in the wavenumber range 400-4000 cm^{-1} with a nominal resolution of 4 cm^{-1}.

2) Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) experiments were performed simultaneously on PP/ES to evaluate the weight change and monitor thermal decomposition behavior using Pyris 1 TGA, Perkin-Elmer. Approximately 7 mg of samples, using a platinum pan, were carried out from ambient temperature to 900°C in nitrogen atmosphere with a purge rate of 20 mL/min and the heating rate of 25°C/min.

3) Mechanical Testing

The mechanical properties of the samples were measured by Universal Testing Machine model Instron series 5569 at room temperature. The crosshead speed was 2 mm/min and three samples with dimensions of 150 mm long, 25 mm wide and 5 mm thick were tested for each set.

III. RESULTS AND FINDINGS

A. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of ES, PP and PP/ES biocomposites are shown in Fig. 1. From Table I, the bands at frequency 3000–2800 cm^{-1}, 1455 cm^{-1} and 1375 cm^{-1}, represent the strong absorption bands of polypropylene [17]. The band at 1408 cm^{-1}, 875–873 cm^{-1} and 712 cm^{-1} represents CO_3^{2-} vibration which shows the occurrence of carbonate group in the composite [11], [18]. The composites which exhibit a transmission band at frequency 572–512 cm^{-1}, represent the Ca-O content in the calcinated filler [14].

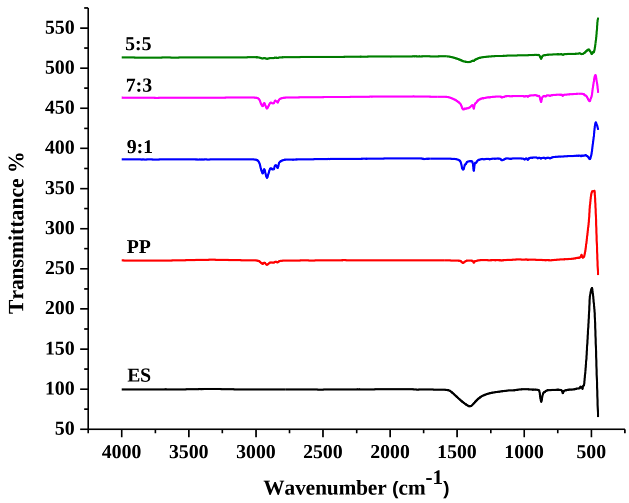

Fig. 1. FTIR spectra of ES, PP and PP/ES biocomposites

Table I: IR band assignments of ES, PP and PP/ES biocomposites

Characteristic band (cm^{-1})	Assignment	References
3000 – 2800	Stretching vibration of C-H	17
1455	Bending vibration of CH_2	17
1375	Bending vibration of CH_3	17
1408, 875 – 873 and 712	CO_3^{2-} vibration	11
572 – 512	Ca-O bonding	14

B. Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermal Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) curves of ES, PP and PP/ES biocomposites are shown in Fig. 2 and Fig. 3 respectively and the results are summarized in Table II. The ES showed only one step of weight loss process, which had a transition temperature that began from 621.04 °C to 893.77°C with a total weight loss of about 42.9313 %. It was clear that the peak transition temperature of ES at 809.62°C due to the loss of CO_2 from the ES carbonate [18].

The thermal decomposition of PP comprises of a two-step process. The first step process that was shown at temperature 238.28°C to 500.96°C had a weight loss of 98.7086 %. The second step of weight loss occurred at 687.56 °C to 746.41°C, with the peak of this transition at 713.40°C. Total weight loss at 713.40°C was around 0.47020 %.

Fig. 2 and 3 also presents the three different weight concentrations (10, 30 and 50 wt. %) of ES on the thermal decomposition of the composites. All the sample material exhibited a two-step degradation process. From Table II, the first step process showed the addition of ES content decreases the weight loss of materials from 89.9543 % to 53.0439 % during the heating time. The second step process showed the maximum peak of the transition temperature for these steps were 738.52°C, 771.53°C and 785.44°C. The percentage of the weight loss composites at corresponding transition was 4.50390 %, 12.5233 % and 20.3375 %. The results showed that the thermal stability of the biocomposites was enhanced as the ES content increases up to 50 wt. % a [4], [8].

TGA and DTA results shows the influence of the ES content on the thermal properties of biocomposite. This analysis proved the addition of calcium carbonate from the eggshell in the sample has increased the thermal decomposition temperature and thus improved the thermal stability of the biocomposites.

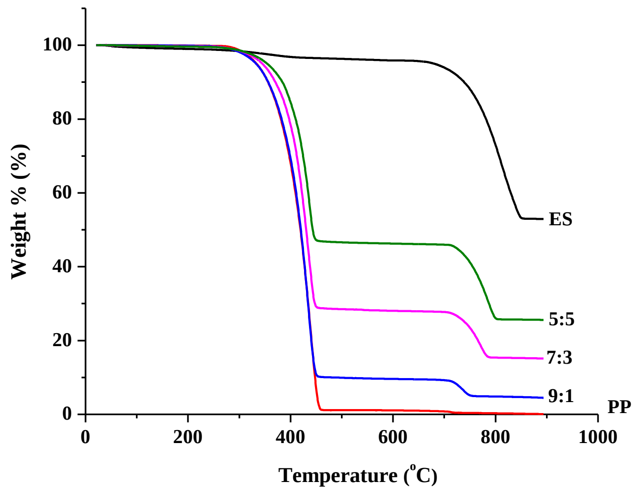

Fig. 2.TGA curves of ES, PP and PP/ES biocomposites

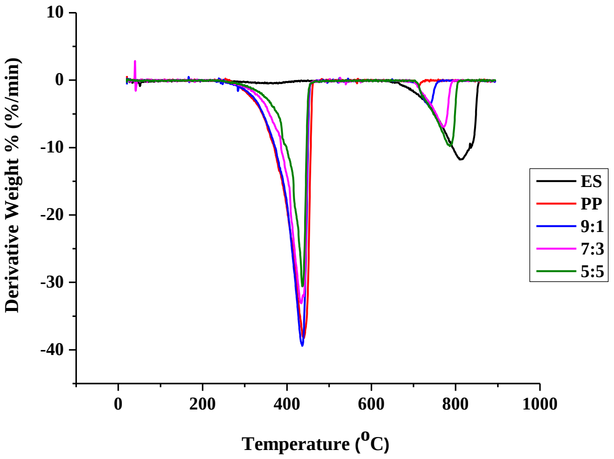

Fig. 3.DTA curves of ES, PP and PP/ES biocomposites

Table II: Thermal analysis data of ES, PP and PP/ES biocomposites

Sample	Step	T_{range} (°C)	Weight Loss (%)	T_{peak} (°C)
ES	I	621.04 - 893.77	42.9313	809.62
PP	I	238.28 - 500.96	98.7086	440.12
	II	687.56 - 746.41	0.47020	713.40
9:1	I	200.96 - 500.96	89.9543	434.61
	II	686.12 - 787.32	4.50390	738.52
7:3	I	234.69 - 500.96	71.1672	437.23
	II	676.79 - 823.21	12.5233	771.53
5:5	I	200.09 - 500.62	53.0439	437.91
	II	681.69 - 836.13	20.3375	785.44

C. Mechanical properties of PP/ES biocomposites

In order to determine the effect of ES as filler content on the mechanical properties, tensile properties were evaluated in terms of tensile strain and tensile stress. As tabulated in the Table III, the tensile strain are found to increase from 0.00769 mm/mm to 0.01658 mm/mm with the increasing of ES content from 10 wt. % to 30 wt. %. However, the values of tensile strain drop slightly to 0.00662 mm/mm as the ES content increased further to 50 wt. % as also observed in a study by Lin et al. [16].

From Table III, the tensile stress of ES content was found increases from 9.718650 MPa to 12.71400 MPa with the increasing concentration of ES from 10 wt. % to 30 wt. % before it start to decrease to 10.90090 MPa at 50 wt. %. This may be due to the fact that an occupation of ES content improves the bonding strength between the polymer matrix and ES [6].

Table III: Mechanical properties of PP/ES biocomposites

SAMPLE (PP:ES)	Load at break (N)	Maximum Load (N)	Tensile Strain (Extension) Maximum Load (mm/mm)	Tensile Stress at Maximum Load (MPa)
9:1	1214.831	1214.831	0.00769	9.718650
7:3	1387.658	1589.250	0.01658	12.71400
5:5	1293.360	1362.612	0.00662	10.90090

IV. CONCLUSION

The results of this study showed that ES reinforcement as biofiller has improved the tensile stress and tensile strain of the composite. The thermal degradation of the prepared composite at different ratios has enhanced its thermal stability as compared to pure PP since they were degraded at higher temperature. The best ratio to prepare the green eggshell/polypropylene biocomposite is at PP:ES (7:3). In future work, the biodegradability of the prepared biocomposites should be investigated prior to explore its potential uses as consumer end product as well as industry applications.

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