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Thermo-mechanical characteristics, performance, and morphological analysis of green eggshells/ polypropylene composites

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Abstract. The global consumption of plastics is projected to triple, reaching 1,231 million tons by 2060. Managing such vast quantities of plastic waste poses significant environmental challenges. Researchers worldwide have been working on reinforcing plastic with biodegradable materials to address these issues. Between 2002 and 2024, over 2000 studies on bio-plastic composites were conducted across over 85 countries. This study used chicken eggshells, a novel bio-filler material, to reinforce polypropylene (PP), one of the most commonly utilized plastics. Eggshells (Es) were incorporated into PP at varying weight percentages (10%, 20%, and 30%) and processed using injection molding and compression techniques. The effects of Es on the mechanical properties of PP, including tensile strength, tensile modulus, elongation at break, flexural strength, and flexural modulus, were systematically evaluated. Additionally, thermogravimetric analysis (TGA) and its derivative (DTG) were employed to assess the thermal stability of both the filler and the composites. Scanning electron microscopy (SEM) was used to investigate the morphology of Es flakes, the eggshell membrane, and the bonding behavior between Es and PP. The findings revealed that incorporating 30 wt.% Es improved the flexural modulus and tensile modulus of PP by 32% and 12%, respectively, while maintaining the flexural strength of pure PP across all tested Es weight percentages. Thermal analysis demonstrated that Es enhanced the thermal stability and reduced the flammability of PP. SEM analysis confirmed strong bonding between the Es membrane and PP and effective interfacial adhesion between the Es outer layer and PP. These results underscore the potential of eggshells as a sustainable bio-filler for improving polypropylene's mechanical and thermal properties.

Keywords: eggshells; Es; DTG; flexural properties; green composite; mechanical properties; tensile properties; TGA; thermal behavior; PP

1. Introduction

Nowadays, the amount of used plastics in industries is vast. In 2019, their waste was 460 Mt, and

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it is forecasted to triple to 1231 Mt by 2060 (OECD, 2022). Certain types of these plastics need over 100 years to fully decompose occupying wide areas around the world (Karan *et al*. 2019). Discarding these materials by incineration would produce huge amounts of carbon dioxide causing environmental pollution (Jang *et al*. 2020). For this reason, researchers worldwide have been trying to reduce the plastics' usage by reinforcing them with biodegradable materials which can be either organic or inorganic, to enhance or at least maintain their mechanical and thermal properties. In this regard, there are more than 1874 articles related to bio-plastic composites published in 85 countries between 2002 and 2022 (Abrha *et al*. 2022). For example, AL-Oqla (2017) tried to improve the mechanical properties of polyethylene matrix with biodegradable pine and cypress. Moreover, Al-Oqla *et al*. (2019) improved the mechanical properties of polymer matrices by using different Jordanian biodegradable fibers such as olive stem, palm stem, and lemon stem. Al-Oqla (2021) declined the weight percentages of low-density polyethylene (LDPE) by 40 % utilizing green olive leaves. Besides, coupling LDPE with olive leaves enhanced their flexural properties, particularly flexural modulus, which increased by 200%. The waste of date palm leaflets is another organic material incorporated with polypropylene to decrease its wt.% and improve its mechanical and thermal properties (AL-Oqla *et al*. 2022). More recently, after 2022, many studies have also been published about the effect of biodegradable fillers on plastics. For instance, the effect of hemp and sisal fibers on the tensile strength of PP was studied using a statistical framework (Al-Shrida *et al*. 2023). Furthermore, various wt.% of pomegranate peel powder, short corn leaves, lemon leaves, and fig leaves were coupled with PP to strengthen their mechanical and thermal properties. Their outcomes discovered Positive impacts of those fibers on the mechanical and thermal properties of PP were obvious at a certain wt.% (Al-Oqla *et al*. 2024, Bendjillali *et al*. 2022). Apart from bio-organic materials, some bio-inorganic materials, like chicken eggshells (Es), can be used to decrease the consumption of polymer while enhancing the properties of the material at the same time (Chfat *et al*. 2024). Eggshells are classified as a bio-ceramic material and comprise a membrane that makes up around 10–11 wt.% of the total weight of the egg. The shell itself is mainly made up of calcium carbonate, which forms about 95% of the structure (Hayajneh *et al*. 2021). Structurally, the outer layer of the eggshell is constructed in three distinct layers: the cuticle, the testa, and the mammillary. The cuticle is considered the outermost protective layer of the eggshell that prevents the penetration of microbes. The intermediate layer, the testa, is primarily composed of calcium carbonate. The innermost layer, known as the mammillary, is covered by the eggshell membrane, which consists mainly of a network of proteins (Mittal *et al*. 2016).

Chicken eggshell is considered one of the most food waste in the world where the quantity of its annual waste hits 8.58 million metric tons according to the statistics in 2018 (Waheed *et al*. 2020). Disposing of such tremendous amounts of waste eggshells in landfills makes it an environmental problem throughout the world. To gain a better understanding, Es produces ammonia gas (NH_3) with pungent foul odors. In addition to ammonia, amines, and hydrogen sulfide (H_2S) are also produced from waste eggshells (Owuamanam and Cree 2020). Besides, the huge piles of eggshell waste can be a shelter for insects, rats, and mice. Apart from environmental problems, eggshell waste further can cause health problems. To exemplify, the residents who are susceptible to low levels of H_2S suffer from respiratory diseases, and eye and nasal symptoms (Legator *et al*. 2001). Regardless of the environmental and health effects, the disposing of Es is costly where it costs more than 250000 dollars per year in the US, the UK, and Europe (Owuamanam and Cree 2020).

Eggshells have several merits. Their density is, for example, relatively low (2.5 g/cm3, Hayajneh *et al*. 2019) when compared with other natural inorganic reinforcement materials like talc (2.8 g/cm3, Huang *et al*. 2020). In addition, eggshells are an environmentally friendly reinforcement.

Bio-waste from Es, in comparison with the bio-dumped lignocellulosic fibers like date palm surface fiber (Ali and Alabdulkarem 2017), sisal fiber (Agarwal *et al*. 2021), and kenaf core (Ahmad Saffian et al. 2020), has higher thermal resistance (Sanmuang *et al*. 2008). Besides the physical and thermal advantages, the cost-effectiveness of Es is another benefit.

Eggshells have been extensively utilized as a filler material, not only in metal matrices (Hayajneh *et al*. 2019, Almomani *et al*. 2020) but also in polymers. Numerous studies have explored the influence of incorporating Es into polymer matrices, including both thermoset and thermoplastic types, on their mechanical and thermal properties. For instance, Toro *et al*. (2007) examined the mechanical response of a polypropylene (PP) matrix filled with varying Es contents (10, 20, 30, 40, 50, and 60 wt.%) and particle sizes (125, 250, and 400 mesh), focusing on properties such as Young's modulus and impact strength. Similarly, Hassan *et al*. (2012) studied the effects of Es on polymer performance. The study utilized varying concentrations (10, 20, 30, 40, and 50 wt.%) of carbonized and un-carbonized Es to reinforce a polyester matrix and investigated the resulting mechanical properties. The results showed that both types of Es' compressive strength and hardness were improved for all concentrations; however, carbonized and un-carbonized Es showed different behaviors for flexural strength and impact energy. More specifically, fresh (un-carbonized) Es continually increased flexural strength up to 40 wt.%, while carbonized Es improved up to 20 wt.%. A similar trend was observed in the impact energy test. Further studies have expanded on the use of Es in composites. Hassen et al. (2015) focused on a composite containing 30 wt.% powdered Es and polypropylene (PP), evaluating its mechanical and thermal properties. Similarly, other researchers such as Panchal *et al*. (2021) investigated epoxy resin's mechanical and erosive performance, incorporating different concentrations (1, 2, 3, and 4 wt.%) of Es nanoparticles. According to their findings, the addition of Es nanoparticles increased the tensile strength, tensile modulus, flexural modulus, and wear resistance of epoxy, with the highest improvements achieved for all the properties at or below 2 wt.% filler loading. The flexural strength showed a maximum at 3 wt.% and decreased with higher concentrations due to nanoparticle agglomeration, whereas hardness continuously improved with increasing Es content.

Panchal *et al*. (2018) studied the addition of boiled and un-boiled Es powder (~300 μm) at different concentrations, namely 4, 8, and 12 wt.%, to an epoxy resin matrix. The authors reported that a composite with the addition of 4 wt.% un-boiled Es showed the best erosion performance. Moreover, the erosion rate for composites with boiled Es was higher compared to the ones with un-boiled Es. Similarly, Shin *et al*. (2020) investigated the properties of two different particle sizes of 100 and 150 μm Es powder at different concentrations of 10, 20, 30, and 40 wt.% within an epoxy-glass fiber composite. They showed that an increase in the Es content lowered the tensile strength, but it remained above the unmodified epoxy-glass fiber composite. Besides, a decrease in the tensile modulus was also observed at all concentrations, except at 40 wt.%. Conversely, compressive modulus generally improved upon the addition of 10 wt.% Es regardless of the particle size.

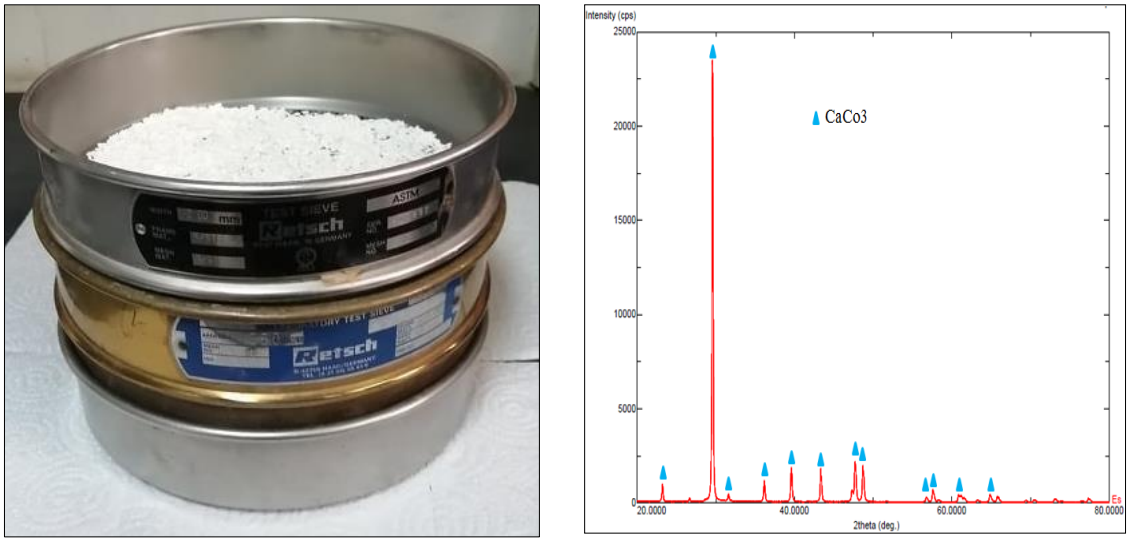
Recently, McGauran *et al*. (2020) compared the effects of fresh and incinerated Es at different weight percentages (5, 10, 25, 40, and 55 wt.%) on the tensile, flexural, and impact properties of composites. The results showed that, regardless of type or concentration, Es reduced tensile strength while increasing tensile modulus. In terms of flexural properties, the flexural modulus increased at all concentrations except at 55 wt.%. However, at 55 wt.%, the impact strength for both types of Es decreased. In another related work, Wu *et al*. (2020) added various concentrations (10, 20, 30, 40, and 50 wt.%) of Es to PVA. According to their results, the tensile modulus of Es increased regularly due to its inherent stiffness. On the other hand, tensile strength and elongation at break decreased at higher concentrations of 40 and 50 wt.%. It also presented improved thermal stability for the

Table 1 Summary of the effects of eggshell on mechanical and thermal properties of polymers properties

Matrix	Filler Size	wt.%	Treatment	Tests	Reference
PP	125, 250 & 400 mesh	10-60 Interval 10%	None	Young modulus Impact strength	(Toro *et al*. 2007)
Ps	NA	10-50 Interval 10%	Carbonization	Flexural strength Impact strength Compressive strength Hardness	(Hassan *et al*. 2012)
PP	100-35 µm	30	Acetic acid (70%)	Tensile strength & modulus Flexural strength & modulus Impact strength Thermal stability	(Hassen *et al*. 2015)
E	~300 µm	4-12 Interval 4%	Boiling	Erosion resistance	(Panchal *et al*. 2018)
E-GF	150 & 200 µm	10-40 Interval 4%	None	Tensile strength & modulus Compressive strength & modulus	(Shin *et al*. 2020)
PP	NA	5, 10, 25, 40 & 55%	Incineration	Tensile strength & modulus Flexural strength & modulus Impact strength	(McGauran *et al*. 2020)
PVA	< 25 µm	10-50 Interval 10%	None	Tensile strength & modulus Elongation at break	(Wu *et al*. 2020)
E-GF-HF	700 nm	7-21 Interval 7%	None	Tensile strength Flexural strength Impact strength Shear strength	(Bhoopathi and Ramesh 2020)
Epoxy	< 500 µm	5-20 Interval 5%	None	Tensile strength Flexural strength Impact strength	(Azman *et al*. 2020)
E	Nanoparticle	1-4 Interval 1%	None	Tensile strength & modulus Flexural strength & modulus Hardness Erosion rate	(Panchal *et al*. 2021)
R-LDPE	76 nm	2-12 Interval 2%	None	Tensile strength, Flexural strength, Impact strength, Hardness	(Bello *et al*. 2021)

obtained Es-PVA composites by applying thermogravimetric analysis.

Furthermore, Bhoopathi and Ramesh (2020) studied the effect of different wt.% (7, 14 & 21) of Es on mechanical properties of (epoxy-glass fiber- hemp fiber hybrid composite). They found that increasing the wt.% of Es led to a decrease in tensile and shear strength. Oppositely, increasing the wt.% of Es causes an increase in flexural strength and impact energy. Moreover, Azman *et al*. (2020) reinforced the epoxy thermoset by three wt.% (5, 10, 15 & 20) of Es particles. The tensile strength of the produced composites decreased continuously with the decrease of wt.% of Es while the tensile modulus increased at all wt.% except at 20. The flexural strength exhibited a decline at 5 wt.% and 10 wt.%, followed by an increase at 15 wt.%, before ultimately decreasing once more at 20 wt.%. A similar trend was observed in the flexural modulus. In summary, Es enhanced thermal stability alongside the mechanical properties. In addition, Bello *et al*. (2021) modified recycled low-



(a) (b)

Fig. 1 (a) Confining the Es flakes between two sieves (850-2000) µm, (b) X-ray diffraction of Es

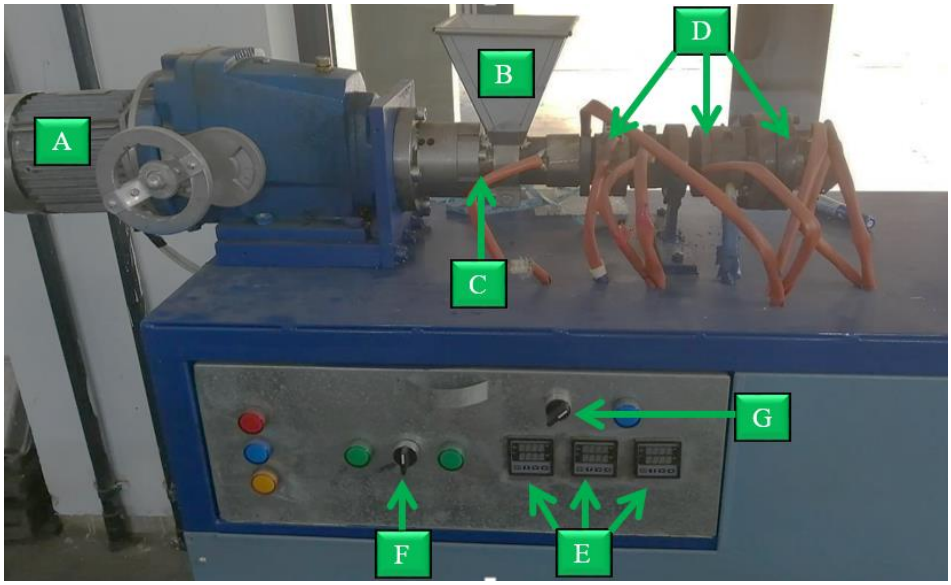
density polyethylene composites (R-LDPE) from different wt.% (2, 4, 6,8,10 & 12) of Es nanoparticles. The findings indicated that the overall weight percentage of Es nanoparticles contributes to an improvement in both bending strength and hardness. Additionally, tensile strength exhibited a continuous increase, except for the highest weight percentage. Impact energy increased up to 6 wt.% before experiencing a decline.

Extensive literature has indicated that the majority of works have only focused on the mechanical performance of these composites. Limited attention was given to the thermal characteristics of such composites. In addition, most prior studies mainly used Es in their powdered forms. To address these gaps, the present study aims to integrate various weight percentages (10%, 20%, and 30%) of Es flake waste and their membranes into a polypropylene matrix. This approach seeks to mitigate environmental pollution while simultaneously improving the thermal and mechanical properties of the composite.

2. Materials and methods

2.1 Materials

Polypropylene matrix was supplied as granules from Saudi Arabia (SABIC Company). Since the surface area of filler plays a key role in the properties of materials (Hassen *et al*. 2015), the current research is going to use Es filler in the form of flake rather than the common powder form. This form of Es, i.e. the flake form, has not been used in the previous studies based on our knowledge. Regardless, the preparation of chickens' eggshells to be used as filler was passed through several steps. First, Es were received from a local farm. Then, the shells were rinsed with water to remove the remainder of the albumen, yolks, and the stinky smell. After that, the wetted shells were dried in the sun. The eggshells were mechanically pulverized into smaller flakes that were further sieved



Symbol	Part
A	One horse power electrical motor coupled with single screw to perform mixing.
B	A hopper measuring 15 cm × 15 cm is used to facilitate the placement of the mixture.
C	A heated barrel with a diameter of 20 cm and length of 50 cm
D	Three thermocouples controlling three zones.
E	Three controllers for the thermocouples.
F	A switch for the electrical motor.
G	A switch for the thermocouples.

Fig. 2 Specialized made injection machine

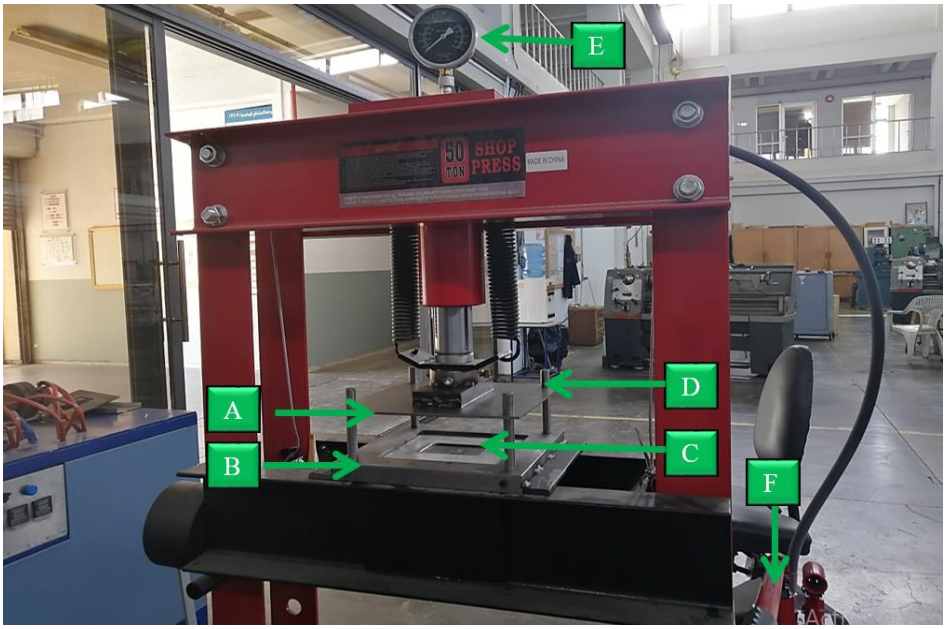
with the aid of two mesh sizes, 850-200 microns as shown in Fig. 1(a). X-ray diffraction analysis indicated that the eggshell is predominantly made up of calcite, as revealed in Fig. 1(b), and is in agreement with the work of Onwubu *et al*. (2019) and Adamu *et al*. (2024). The eggshells used were in their natural state and did not undergo any chemical treatment, according to the methodologies provided by Chong *et al*. (2020) and Wei Chong *et al*. (2023). The density of the eggshells was previously measured in our earlier study (Hayajneh *et al*. 2019) and found to be 2.5 g/cm.

2.2 Samples preparation

PP granules were mixed manually with three weight percentages of Es flakes, namely 10%, 20%, and 30% as described in Table 2. Then, the mixtures were fed into a locally manufactured injection molding machine as shown in Fig. 2, and heated up to a temperature of 180-190 ˚C. Then, the compound was kept mixed for 100 seconds. The compounding was followed by the compression of the samples for 100 seconds in a domestically manufactured compression molding machine shown in Fig. 3. The compression was performed at room temperature and under a pressure of 0.7 MPa. Each sample was replicated three times.

Table 2 Symbols of PP samples

Sample	Es (wt.%)	PP (wt.%)
Bare PP	0	100
PP10Es	10	90
PP20Es	20	80
PP30Es	30	70



Symbol	Part
A	A movable plate to conduct the pressure process.
B	A fixed plate to withstand the applied pressure
C	A mold cavity with dimensions 10×7×4.3 cm
D	Four pins to align the two plates together
E	Pressure gauge
F	A handle to control the movable plate

Fig. 3 Specialized designed compression molding

2.3 Mechanical properties

Tensile and flexural tests were conducted by the ASTM D3039-3039M and ASTM D790 standards, respectively. The specimens for both tests were extracted from a larger sample measuring 100×70×4.3 mm, with the dimensions of the tensile and flexural specimens being (80×15×4.3) mm and (100×10×4.3) mm, respectively. The crosshead speed for the tensile test was established at 2 mm/min, while for the flexural test, it was set at 5 mm/min. Additionally, the gauge length for the tensile test was 50 mm, and the span-to-depth ratio for the flexural test was approximately 16. The samples before the three-point bending test are illustrated in Fig. 3.

Fig. 4 Eggshells composites before flexural test

2.4 Thermal properties

Thermogravimetric analysis (TGA) using the NETZSCH TG 209 F1 Iris was conducted to assess the thermal stability of the Es flake along with its membrane. Additionally, TGA was employed to investigate the influence of Es incorporation on the thermal characteristics of the PP30Es composite. Approximately 25 mg of each sample was analyzed over a temperature range of 35 to 900 ˚C in a nitrogen environment, with a heating rate of 10 ˚C/min.

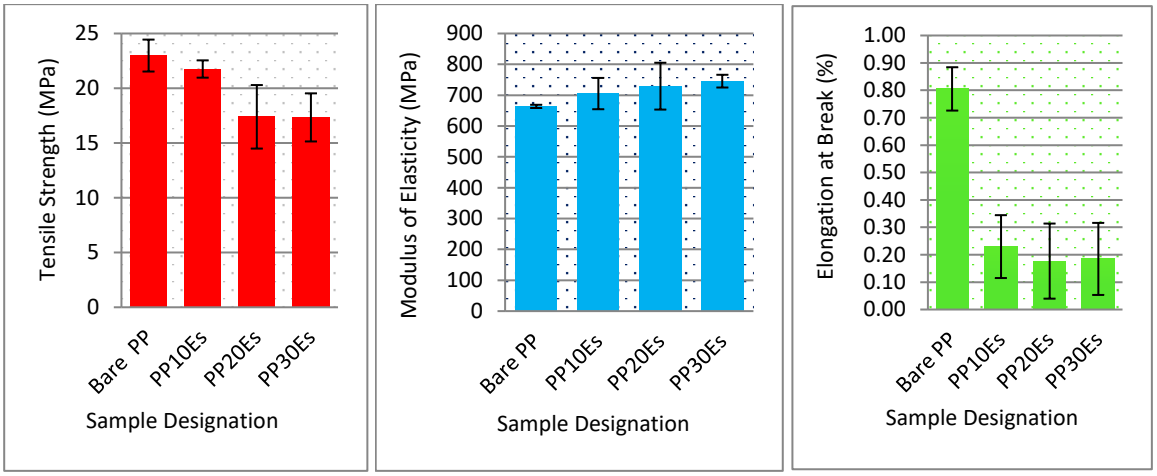
2.5 Scanning electron microscope characterization

The topographical features of both the internal and external surfaces of the Es flakes, along with their membrane structure, were assessed using a Quanta™ 450 FEG scanning electron microscope (SEM). Furthermore, the bonding characteristics at the interface between the Es filler and polypropylene (PP) were examined. In addition to analyzing the distribution of Es flakes within the PP matrix, the type of fracture was characterized following the tensile testing of the PP30Es composite.

3. Results and discussion

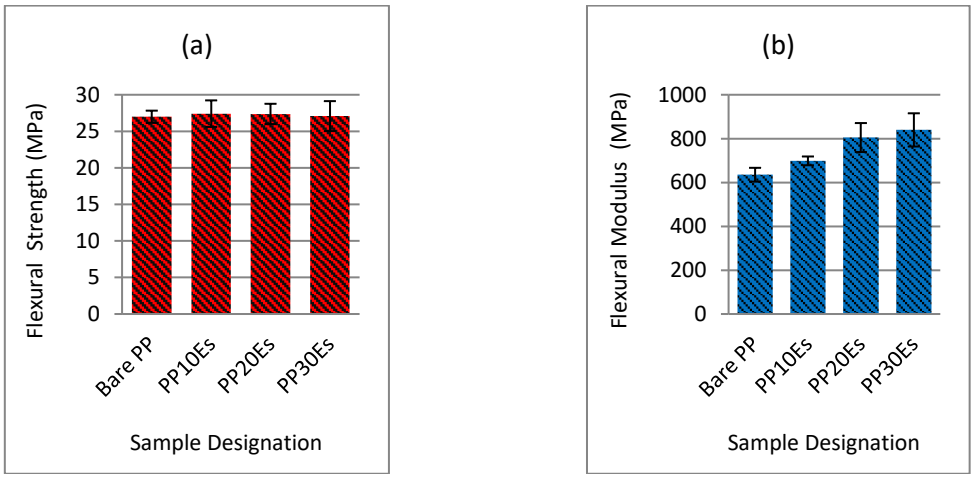
3.1 Tensile test

The variations that happened in tensile properties due to the addition of Es are presented in Fig. 5. It is evident that adding Es to PP has gradually decreased the tensile strength (TS) which is expected due to the stiff bio-calcium carbonate but at the same time the addition of Es has improved modulus of elasticity. Adding 10 wt.% of Es has lessened the TS by 5% whereas it has heightened the modulus of elasticity by 8 %. In comparison, the addition of 30 wt.% of Es has worsened the TS by 25 % but simultaneously it has enhanced the E by 15 % (Fig. 5(a)-(b)). This phenomenon can be attributed to the effective compatibility between the fillers and the matrix, which improves the mechanical properties and performance of the composite through enhanced stress transfer efficiency. This enhancement is primarily due to the strong adhesion between the fillers and the matrix, as detailed in the morphological analysis. However, the composite's tensile strength decreased compared to the original matrix. This reduction is linked to the agglomeration of fillers at high concentrations of eggshell, leading to filler pull-out from the matrix due to inadequate matrix



(a) Tensile Strength (b) Tensile Modulus (c) Elongation at break

Fig. 5 Tensile properties of Es composites



(a) Flexural Strength (b) Flexural Modulus

Fig. 6 Flexural properties Es composites

material to effectively wet the eggshell fillers. Azman *et al*. 2020 obtained a similar conclusion for epoxy composites with eggshell fillers. For the case of elongation at break, neat PP showed the highest value of 0.81%, while embedding PP with 10 wt.% of eggshell reduces this by about 70%, while any further increase in the eggshell weight percentage normally produces continued decreases in the elongation shown by Fig 5(c). The explanation for this behavior is that eggshell fillers are rigid. These findings are consistent with the observations made by Wu *et al*. (2020).

3.2 Flexural test

Figs. 6(a) and 6(b) present the variation of flexural strength (FS) and flexural modulus (FM) of PP by the addition of eggshell (Es) fillers. Fig. 6(a) shows that for all weight percentages, no

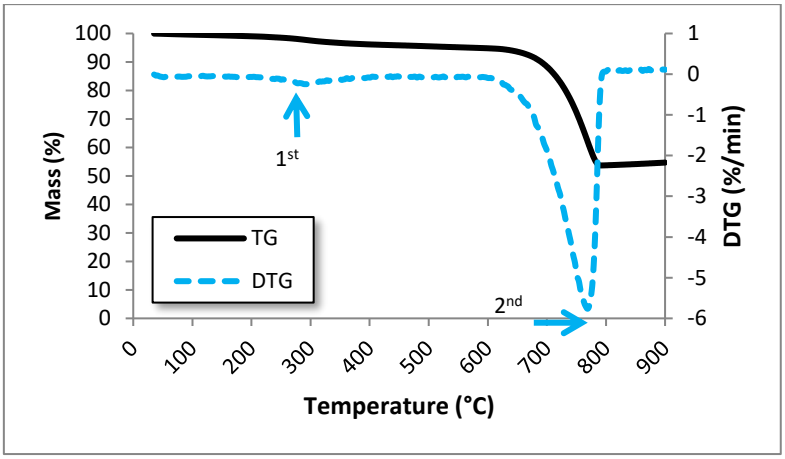


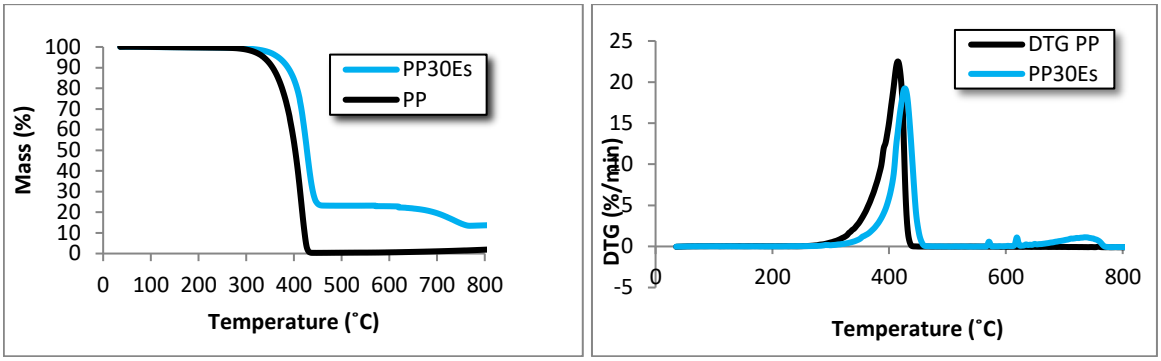
Fig. 7 TG and its derivate (DTG) thermogram of Es filler

improvement in FS was achieved by the Es fillers; however, it contributed to the stabilization of FS values while achieving a 30% reduction in the use of thermoplastic PP. In contrast, the addition of Es fillers significantly improved FM values, which increased linearly with the Es weight percentage. At a filler content of 30 wt.%, the FM was improved by about 32% (Fig. 6(b)). The addition of eggshell fillers to polypropylene ensured the effective transfer of stress in the composite when subjected to applied loads without the development of any form of stress concentration or risers in the polymer matrix. There was good adhesion between the fillers and the matrix, as evidenced by the significant improvement in the flexural modulus of the composites. This was also evidenced by the scanning electron microscopy (SEM) studies. A similar trend was observed by McGauran *et al*. (2020).

3.3 Thermogravimetric Analysis (TGA)

3.3.1 TGA/DTG of Es Filler

Fig. 7 shows the TG and DTG curves of the eggshell filler, Es, reflecting two distinct stages of mass loss. From the TG curve, it is observed that the first mass loss, which is about 1.5%, occurred at ~230°C and is attributed to the decomposition of the organic Es membrane. This is in agreement with the work of Na *et al*. (2020), who reported the decomposition of the Es membrane at a similar temperature. A starting temperature of 640°C is observed for the second stage of mass loss with only 5% from its original mass lost. The result indicates the filler thermal stability for reinforcing the PP matrix because of withstanding the processing temperature of the composites. At this endset temperature, it was observed that the degradation was completed at 785°C and 46% mass loss. It is worth noting that $T_{50\%}$ does not exist since the decomposition of the Es filler ends before attaining this value. The confirmation of the thermal stability of the Es filler is also obtained by the char residue above 600°C, which is about 95%. The TGA results for the Es filler and its organic membrane indicate that both are stable in the course of the fabrication process of PP-Es composites at processing temperatures of 180–190°C. The DTG curve gives the maximum degradation temperature, T_{max}, which is the temperature corresponding to the maximum mass loss rate. It presents two distinguished peaks: the first peak, at ~300°C, corresponds to the decomposition of the organic membrane, while the second one, at ~762°C, refers to the conversion of calcium carbonate, CaCO3, into calcium oxide, CaO. This result agrees with the study of Rohim *et al*. (2014).



(a) TG thermogram of PP and PP30Es composite

(b) DTG thermogram of PP and PP30Es composite

Fig. 8 Thermal properties of PP matrix and PP30Es composite

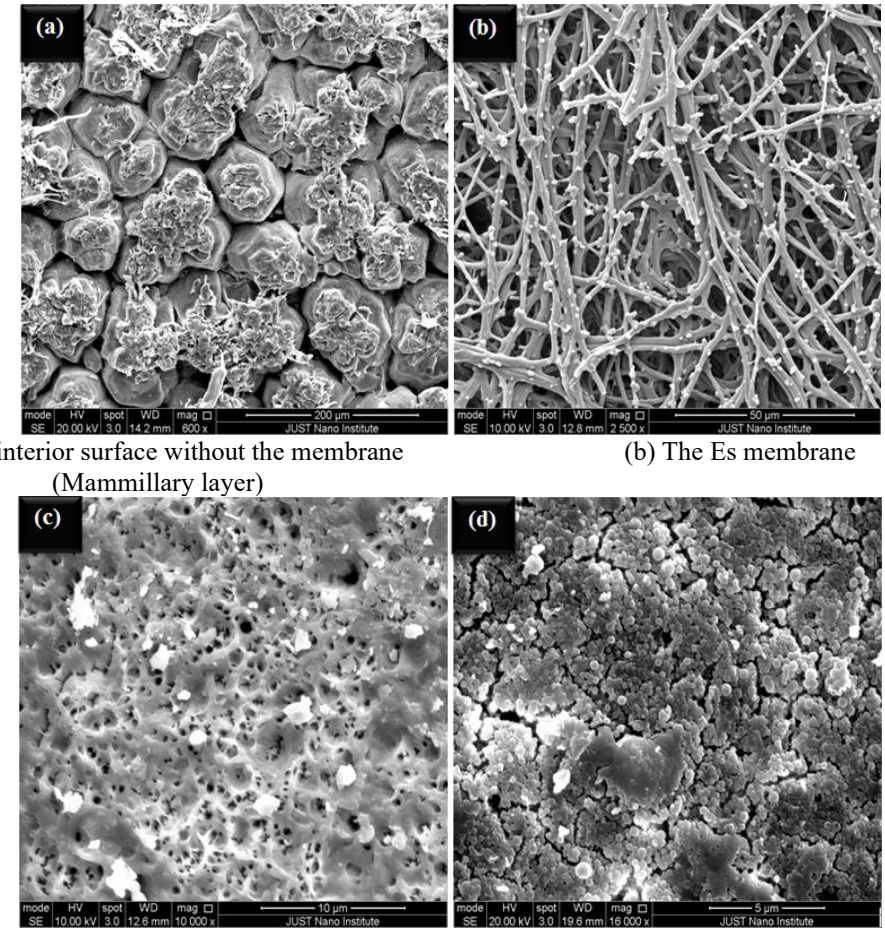
Table 3 TG and DTG data for Es, Bare PP and PP30Es composite

Sample	T_{onset}(˚C)	$T_{50\%}$ (˚C)	T_{endset} (˚C)	T_{max} (˚C)	Residue after 600 ˚C (%)
Es	640	-	785	760	95
PP	321	403	430	410	~ 0
PP30E	329	428	449	427	23
Sample	T_{onset}(˚C)	$T_{50\%}$ (˚C)	T_{endset} (˚C)	T_{max} (˚C)	Residue after 600 ˚C (%)

3.3.2 TGA/DTG of PP matrix and PP30Es composite

Fig. 8 presents the thermogravimetric curves and derivative thermogravimetric curves of both PP and PP30Es composite. A higher onset temperature was calculated for the PP30Es composite, 329°C, in comparison with the PP matrix, which had an onset of 321°C. This result is in agreement with the reported results by Wu *et al*. (2020) for PVA-Es composites. Moreover, the endset temperature rose to 449°C in the case of the PP30Es composite, compared with 430°C for the PP sample. Significantly, almost no char residue was yielded in PP after 600°C, whereas about 23% was retained in PP30Es composite. From the literature, Onwobu *et al*. (2019) have reported that CaCO3 decomposing to CaO at temperatures beyond 760°C is responsible for the presence of char residue in PP30Es composites. From the TG curve, the initial degradation temperature (T_i), the temperature at 50% mass loss ($T_{50\%}$), and the final degradation temperature (T_f) of PP30Es were all higher than those of PP. These results indicate that the incorporation of Es filler significantly enhances the thermal stability of the PP matrix.

Fig. 8(b) presents the DTG curve, indicating different degradation behaviors of PP and the PP30Es composite. In the case of PP, the curve indicates a single-step degradation process. By contrast, the PP30Es composite undergoes a two-step degradation process in which the first step corresponds to the degradation of PP, and the second step is attributed to the transformation of Es into CaO. The addition of Es into the PP matrix shifted the DTG peak from 410°C for PP to 427°C for PP30Es, as shown in Fig. 8(b). Meanwhile, the mass loss rate was decreased by the addition of Es, as revealed by the shorter peak in the DTG curve. All these further demonstrated that the addition of 30 wt.% Es improved not only the thermal stability of PP but also its low flammability. A summary of the thermal properties in detail is given in Table 3.



(a) The interior surface without the membrane (Mammillary layer)
(b) The Es membrane
(c) The exterior surface of Es without a Cuticle layer (Testa layer)
(d) Cuticle layer covers Testa layer

Fig. 9 SEM micrographs of Es flake

3.4 Morphological analysis

3.4.1 The morphology of Es filler

Fig. 9 shows the morphology of the inner surface of the Es flake, both with and without the membrane (Fig. 9(a) and Fig. 9(b), respectively). It also displays the morphology of the Testa layer (Fig. 9(c)), which is covered by the cuticle layer, providing a protective barrier against microbial invasion (Fig. 9(d)). In Fig. From Fig. 9(a), the Es membrane is revealed to be of a porous and fibrillar protein structure, which is very important for its adhesion to the PP matrix as will be discussed in the following section. In contrast, the inner surface of the Es flake without the membrane is found to be quite rough, which may negatively affect its adhesion to the polymer matrix. Furthermore, the spongy texture of the outer surface of the Es flake, known as the Testa layer (Fig. 9(c)), is different from that of the Es membrane (Fig. 9(b)), Mammillary layer (Fig. 9(a)), and Cuticle layer (Fig. 9(d)). Such structural differences result in different bonding behaviors. The presence of impurities on the outer surface, which probably has a negative effect on filler-matrix adhesion, may also be seen from the SEM micrographs presented in Fig. 9(c-d).

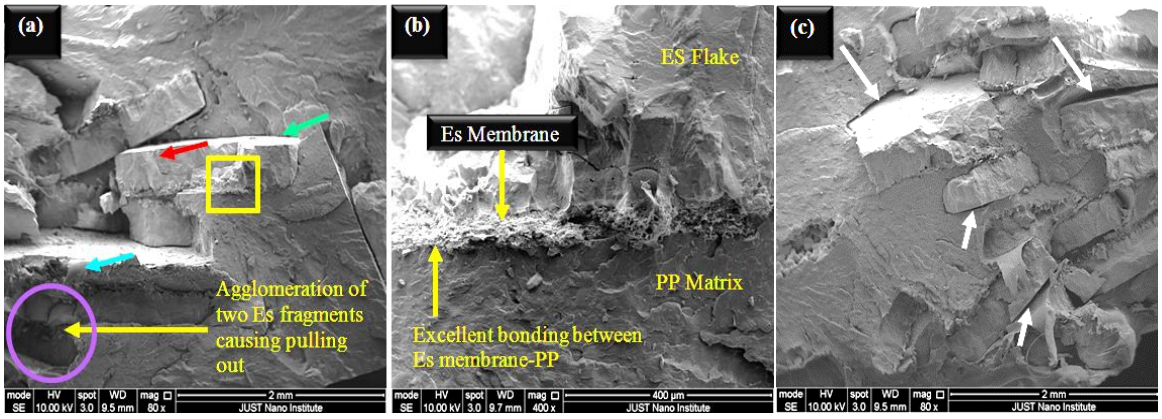


Fig. 10 SEM micrographs of PP30Es composite. (b) is a magnification for the yellow square in micrograph (a), while (c) is another micrograph to illustrate more detail. Red and blue arrows show the fracture behavior. Green and yellow arrows represent the bonding behavior. White arrows indicate the tendency of Es outer surface to detach. Purple circle displays pull-out event

3.4.2 The surface morphology PP30 Es composite after tensile test

Fig. 10 shows the morphology of the fracture region after the tensile test. It can be seen from the image that the eggshell flakes have aggregated in some places, as shown by the purple circle in Fig. 10(a). There are gaps where the PP fails to encapsulate the Es flakes completely, as indicated by the yellow arrow in Fig. 10(a). This agglomeration could be due to two factors: the short mixing time of PP and Es during processing in the injection machine and the high concentration of Es flakes, which was 30 wt.%. Agglomeration of Es flakes promotes the pull-out phenomenon, which may reduce the mechanical properties by decreasing the efficiency of the stress transfer between the matrix and filler. Specifically, the Es agglomeration observed in 30 wt.% composites may reduce the tensile strength because of the insufficient wetting matrix for Es fillers, which may lead to a pull-out phenomenon and a reduction in the efficiency of internal stress transfer within the matrix. Also, the naturally brittle nature of the Es flakes would contribute to the characteristics of the brittle fracture in Es-PP composite where proper compatibility and adhesion between the filler and matrix exist, as represented for the studied composites in Fig. 10 (a), whereas ductile fracture within the PP matrix is pointed out in Figs. 10 (a) to (c) by a blue arrow. Figure 10 clearly shows that there is a clear difference in the interfacial bonding characteristics between the internal and external surfaces of the Es flake, including the Es membrane. The external surface of the Es shows strong adhesion with the PP matrix, as indicated by the green arrow in Fig. 10(a). In contrast, much stronger interfacial bonding is observed for the Es membrane, as presented in Fig. 10(b). Closer scrutiny of Fig. The detachment of the Es flake in 10(c) initiates at the outermost surface without the membrane, proving that the adhesion at the external surface is weaker than at the internal surface with the membrane marked with white arrows in Fig. 10(c).

4. Conclusions

In this study, the thermo-mechanical characteristics, performance, and morphological analysis of green eggshells/polypropylene composites were comprehensively examined to assess their viability

as sustainable material alternatives. The research explored the incorporation of green eggshells, a renewable and waste-derived filler, into polypropylene matrices, aiming to improve the composite's mechanical properties while maintaining or enhancing its thermal stability. Through detailed analysis, this study provides valuable insights into the potential of green eggshells as a functional filler in polymer composites, highlighting their role in improving material performance while contributing to environmental sustainability. The key findings of this research are summarized as follows:

• Adding Es improved the flexural and tensile moduli of PP. Specifically, the addition of 30 wt.% Es resulted in a 33% increase in flexural modulus and a 12% increase in tensile modulus.

• While Es improved moduli, it reduced tensile strength. At 30 wt.% Es, tensile strength declined by 25%.

• Eggshell flake significantly enhanced the thermal stability of PP composites. The DTG peak temperature of PP shifted from 410°C to 427°C with the addition of 30 wt.% Es, and the char residue increased, indicating better heat resistance.

• The incorporation of Es did not alter the flexural strength of PP but contributed to reducing the quantity of synthetic PP used.

• Morphological studies revealed strong bonding between the Es membrane and PP, while the outer Testa layer of Es showed good bonding but weaker adhesion compared to the inner membrane.

• Thermal analysis confirmed that Es flakes are stable under processing conditions (180-190°C) and that they reduced the flammability of PP composites.

• Incorporating eggshells (Es) as a bio-filler in polypropylene (PP) composites helps mitigate environmental issues by reducing plastic and eggshell waste, which are major sources of pollution.

• Using Es as a filler is a sustainable and cost-effective method for improving polymer properties while addressing the disposal problems associated with eggshell and plastic waste.

Abbreviations

Es	Eggshells	Ps	Polyester
PP	Polypropylene	E-GF-HF	Epoxy-Glass fiber-Hemp composite
PP10Es	Polypropylene-10 wt.% of Eggshells Composite	TS	Tensile strength
PP20Es	Polypropylene-20 wt.% of Eggshells Composite	FS	Flexural strength
PP30Es	Polypropylene-30 wt.% of Eggshells Composite	FM	Flexural modulus
PVA	Poly (vinyl alcohol)	TGA and DTG	Thermogravimetric analysis and its derivative
LDPE	Low-density polyethylene	T_{onset}	The temperature at which the material begins to thermally decompose
R-LDPE	Recycled low-density polyethylene	T_{endset}	The temperature at which the material ends the thermal decomposition
GF	Glass fiber	T_{max}	The temperature at which the mass loss rate touches the highest point
HF	Hemp fiber	$T_{50\%}$	The temperature when the mass loss is 50 %
E	Epoxy	NA	Not available

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