

PAPER 83 – A REVIEW OF THE EFFECT OF EGGSHELL POWDER ON THE PROPERTIES OF RECYCLED POLYMERS

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ABSTRACT

Agricultural wastes have become a major source of environmental pollution as they have been implicated in the formation of greenhouse gases. Eggshell is a poultry waste that is available in large quantities and the disposal of has become a cause of pollution due to the generation of unpleasant odours and growth of microorganisms of which 6.4 million metric tonnes of eggshell waste are dumped globally in landfills. This paper reviews the effects of incorporating eggshell powder (ESP) on the properties of recycled polymers. It covers the preparation and characterisation of eggshell powder, its incorporation into recycled polymers, and the resulting changes in mechanical and thermal properties. In recycled low-density polyethylene, a maximum tensile strength of 10.64Nm⁻² was obtained at 10wt. % of ESP after which the tensile strength decreased at 12 wt%. For recycled High-density Polyethylene/ethylene vinyl acetate (rHDPE/EVA) composite, a decrease in elongation at break and tensile strength were obtained with increasing ESP filler loading. However, the addition of a coupling agent (3- aminopropyltriethoxysilane) resulted in higher tensile strength and modulus. Another coupling agent (Benzyl Urea) was used on rHDPE/EVA composite and a significant improvement in tensile strength and modulus of elasticity was obtained.

KEYWORDS: Eggshell powder, Recycled polymers, Environmental pollution.

1. INTRODUCTION

Recycling polymers is a way to mitigate the environmental menace caused by heaps of polymeric waste produced from a continued increase in the consumption of polymers (mainly plastics) (Achilias et al., 2007) and also conserve natural oil and gas from which these polymeric materials are made (Hamad et al., 2013). The Food and Agriculture Organization of the United Nations (FAO) reported that landfills worldwide received 6.4 million tons of eggshell. This statistical information suggests that there is a significant opportunity to recycle and repurpose eggshell in polymer products (Bhagavatheswaran et al., 2019). The use of eggshells as an additive for concrete has been established (Hamada et al., 2020). Due to its rich CaCO₃ content which is a hard mineral (Ho et al., 2013), eggshell powders (ESP) are possible strengthening additives for recycled low-density polyethylene (rLDPE) composites which are lightweight and a potential automobile component (Bello et al., 2021). This paper is focused on reviewing recycled High-density polyethylene/ Eggshell powder (rHDPE/ESP) composite with their properties evaluations to establish their future applications.

2. THEORETICAL ANALYSIS

Recycled plastics are different from virgin raw material because it has been processed. This results in some level of deterioration and aggravated characteristics that make the starting raw material base plastic of lower grade properties (Golkaram et al., 2022). Also, the recycled polymers usually don't come from the precise plastic, resulting in incompatibility problems in the recycled plastic mix hence additives are important to improve their properties to make quality products within specifications that make them suitable for a range of applications (Vasudeo et al., 2016). Polymers can be recycled by reuse, mechanical recycling, and chemical recycling. However, reuse is not appreciably practised when it comes to plastics. Plastic products are generally dumped after first use or if reused do not continue for a long time, especially in food applications. A few examples of reuse can be seen in refilled drink bottles with washing liquids or consumers refilling and hence reusing their plastic bottles at home. Mechanical recycling involves grinding, reprocessing, and compounding the plastic to yield a new product that may or may not retain its former use. In chemical recycling, the polymer waste

is converted back into its oil/hydrocarbon component in the cases of polyolefins and monomers in the case of polyesters and polyamides, which can be used as raw materials for new polymer production and petrochemical industry, or into the pure polymers using suitable chemical solvents (Hamad et al., 2013; Khalid et al., 2022; Ncube et al., 2021; Ragaert et al., 2017).

3 METHODOLOGY

3.1 Preparation of eggshell powder

The eggshells were prepared differently by the authors:

Research by Farahana et al. (2014) on recycled high-density polyethylene/ethylene vinyl acetate/eggshell powder (rHDPE/EVA/ESP) cleaned, dried, and ground the eggshell into a fine powder using a kitchen blender to an average particle size of 63 μ m. It was then dried in a vacuum oven at 80°C until a consistent weight was achieved.

Hanif et al. (2020) researched on rHDPE/EVA with uncarbonised and carbonised eggshell powder. The authors washed and dried the eggshell in a conventional oven at 80°C until a constant weight was achieved. The dried eggshells were crushed into smaller pieces and ground into powder using planetary ball mills set at 300rpm for 60 minutes and a kitchen blender. This was sieved to obtain a particle size of 63 μ m to remove coarse particles. A part of the eggshell was carbonised in a muffle furnace at 700°C for approximately 3 hours.

Farm et al. (2022) washed the eggshells and dried them at room temperature for 24 hours, it was ground using a blender and sieved to a mesh size of 32 μ m using a sieve shaker. Carbonised eggshell powder (CESP) was also prepared by thermally treating the eggshell at a low pyrolysis temperature of 400°C for one hour.

Bello et al. (2021) studied the effect of eggshells on recycled low density polyethylene (rLDPE). The eggshell was prepared using three different methods, which are manual crushing, disc grinding, and 70 hours of ball milling.

3.2 Preparation of recycled polymer composites

Farahana et al. (2014) prepared rHDPE composites by melt blending technique in an internal mixer. rHDPE was mixed at 160°C, 50 rpm for 4 minutes. Then, pre-determined quantities of EVA (Ethylene Vinyl Acetate), maleic anhydride (MA) which acted as a compatibilizer to enhance the interfacial interaction between the rHDPE and EVA matrix and ESP with filler loading of 0,5,10,15,20,25 wt.% were added and mixed for an additional 10 minutes. The composite matrix of rHDPE/EVA had a constant composition of 50wt.% each in all formulations. The resulting molten samples were then compressed into 2mm thick sheets using a hydraulic press at 160 °C for 2 minutes and cooled under pressure for 4 minutes.

In a related study by Farahana et al. (2015b), the compatibilizer used was Benzyl Urea (BU) with rHDPE/EVA (50/50 phr) composites. The composite was prepared through melt blending process in an internal mixer at a temperature of 190°C and a speed of 50rpm for 4 minutes. Pre-weighed amounts of EVA, BU, and ESP were then added to the mixer for an additional 6 minutes. The filler loading of ESP was 0,5,10,15,20,25 phr of the matrix composition. The resulting molten samples were compressed into 2mm

-thick sheets using a hydraulic press at a temperature of 190°C for 2 minutes and then cooled under pressure for 4 minutes.

In another study by Farahana et al. (2015a), 3-Aminopropyltriethoxysilane (APTES) was used as a coupling agent with rHDPE/EVA(50/50phr) composites. Melt blending was used to prepare the composites in an internal mixer at 190°C at a speed of 50rpm for 4 minutes. Pre-weighed EVA and ESP (filler loadings of 0,5,10,15,20,25 phr) or treated ESP(5,10,15,20,25 phr) were then added to the rHDPE, and the mixture was blended for another 10 minutes to obtain a homogeneous composite. The composite was then discharged from the mixer, pressed into round pieces and allowed to cool.

Hanif et al. (2020), prepared rHDPE/EVA (70/30) composites by melt blending at a temperature of 160°C within 10 minutes at 50rpm. The composites were prepared by preheating rHDPE pellets for 2 minutes in a mixer, followed by EVA pellets and allowed to mix for 5 minutes. ESP (filler loading of 5-25 wt%) or carbonised ESP (CESP) with filler loading of 5-25 wt% were added afterwards for 3 minutes. The resulting blends were subjected to compression moulding for 10 minutes and cool pressed for 5 minutes.

Farm et al. (2022) prepared rHDPE by first cleaning the containers, cutting them into small pieces then melted in an internal mixer at 175°C at 32rpm. Eggshell powders were added to the melted HDPE at specific ratios for 8 minutes, after which the mixture was crushed and compressed using a hydraulic hot press. The compression moulding process involved preheating at 175°C for 3 minutes, followed by compression for 4 minutes. Each composite sample was prepared with a weight ratio of r-HDPE/filler varied at 90/10, 80/20, and 70/30.

Bello et al. (2021), prepared the rLDPE composites by dissolving 2 wt.% ESP in absolute ethanol, agitating the mixture in a ball mill, adding rLDPE to the mixture, heating and stirring until the ethanol vaporized, thereafter, palm kernel oil was added as a plasticizer after which the mixture was processed using a two-roll polymer mill. The resulting composite sheets were hot pressed and moulded using hydraulic compression to produce various samples for analysis. The process was repeated with increasing weight per cent of ESP up to 12 wt. %.

4 RESULTS AND DISCUSSION

4.1 Mechanical properties

4.1.1 Tensile strength

A study by Hanif et al. (2020) showed that the addition of ESP and CESP fillers decreased the tensile strength of the rHDPE/EVA blend composites. The author proposed the decrease in tensile strength was due to poor filler distribution and low interaction within the matrix. The increased filler concentration impeded good stress transfer between the matrix and the reinforcement filler when external stress was applied. However, rHDPE/EVA reinforced with CESP filler showed superior properties due to the removal of the spongy portion and the subsequent elimination of volatile matters during carbonisation. Results also showed that the tensile modulus increased for both composites when the amount of filler was increased. This was due to the presence of small and rigid filler particles that gave a better reinforcement structure in composites, improving stiffness and reducing the ductility of the blend composites. In general, the rHDPE/EVA/CESP composites had better filler particle dispersion and tended to form smaller agglomerates than the rHDPE/EVA/ESP composites. The author suggested that this was due to any separation in the ESP filler as a result of loose particles being removed when carbonising the ESP.

Farahana et al. (2015b) observed that the incorporation of ESP in the composite decreased its tensile strength and the author suggested that this was due to the non-polar and polar nature of the rHDPE and EVA polymer system, respectively, and the inability of ESP to support stress transfer. However, the addition of BU increased the tensile strength by facilitating stress transfer and improving interfacial adhesion. In a related study by Farahana et al. (2014), the compatibilizer used was maleic anhydride (MA) and results showed that the tensile strength of the composites decreased with increasing ESP content which was proposed by the author to be due to poor interaction force between the components. However, the addition of MA improved the tensile strength by facilitating stress transfer between phases and increasing interfacial adhesion.

The effect of adding ESP filler to rHDPE/EVA matrices was studied by Farahana et al. (2015a) with and without APTES coupling agent and results on the tensile strength showed that the tensile strength of both composites decreased as the concentration of ESP increased due to weak interfacial adhesion. It was suggested that the addition of APTES coupling agent promoted better interfacial adhesion, resulting in improved stress transfer and higher tensile strength.

Bello et al. (2021) studied the effect of eggshell on RLDPE and observed that the addition of ESP increased the tensile strength up to 10 wt% at which tensile strength of 11mm⁻² was obtained after which the tensile strength decreased to a value of 9mm⁻² at 12 wt%, however, this value was higher than pristine rLDPE. According to the author, the increase in tensile strength was due to the structural integrity established by the individual ESP particles acting as load bearers and effectively transferring the load from the RLDPE matrix. The stress localisation is prevented due to the continuous and imperfection-free structure of the composite. Under load, the pores and crazes gradually stretch and fuse, forming cavities of different sizes until necking occurs, and the RLDPE/ESP attains ultimate tensile strength. The increase in the tensile strength with an increase in the wt% of ESP is due to a higher number of particles that offer a higher resistance to deformation before the composite necks. The decrease in tensile strength at 12 wt% is linked with defects and imperfections in the composite. Also, the study found that the tensile strength of rLDPE is comparable to that of pristine LDPE, with a difference of only 4%. The tensile strength of the pristine LDPE was 6.56 ± 0.33 Nmm⁻² while that of rLDPE was 6.31 ± 0.2 nmm⁻².

4.1.2 Flexural strength

A study on the effect of ESP and CESP on rHDPE showed the flexural strength of the composite at various filler loadings (Farm et al., 2022). The result showed that as the filler loading increased from 10 wt.% to 30 wt.% for ESP, the flexural strength increased. This finding is similar to previous research conducted by Siti Shuhada et al.(2009) and Buakaew et al. (2013). Buakaew et al. (2013) found that the maximum flexural strength and modulus for virgin HDPE/ESP were 31.2 MPa and 0.93 GPa, respectively at 30 wt. % of ESP. However, Farm et al. study showed even higher flexural strength and modulus at 32.21 MPa and 2.06 GPa for r-HDPE/CESP at 40 wt.% filler content. The results also showed that the flexural strength of CESP-reinforced r-HDPE is higher than ESP-reinforced r-HDPE. The author suggested that the weak bonding/adhesion between the matrix and filler was attributed to the lack of chemical modification. The optimal filler loading was found to be 20wt.% for ESP and 30wt.% for CESP, beyond which agglomeration resulted in poor wetting and decreased stiffness.

The study of flexural strength for rLDPE by Bello et al. (2021) showed a higher value for rLDPE/ESP composite than pristine rLDPE polymer. An increase in flexural strength of up to 12 wt% was observed, with a slight decrease at 6 and 8 wt% ESP addition. The author proposed that the increase in flexural strength is attributed to the stiffening effect of eggshell nanoparticles, which form barriers that delay or block craze advancement during flexural loading. The addition of ESP creates multiple barriers that require additional stress for craze movement, resulting in higher flexural strengths of the rLDPE composites compared to the pristine rLDPE polymer. The number of barriers created by ESP is dependent on their weight fraction, with an expected increase in the number of barriers at higher weight fractions. However, the slight decrease at 6 and 8 wt% could be due to defects that cause discontinuity in the composites and reduce the degree of ESP networking within the matrix, leading to the composite's deformation at lower stress than expected.

4.1.3 Impact strength

Bello et al. (2021) research showed that the impact energy of the rLDPE composite decreased above 6 wt% ESP addition, which is a trade-off for an increase in hardness values, as harder materials absorb less impact. It is established that ESP addition to rLDPE increases impact energy up to 6 wt% while maintaining the hardness value of pristine rLDPE. However, above 6 wt%, there is a discernible improvement in the hardness of the composite. The author backed his findings with previous research that shows improvement in mechanical properties due to ESP addition. The author also proposed that the increase in impact energy up to 6 wt% could be attributed to the interaction between rLDPE and CaCO₃ of ESP, resulting in a less hard/soft structure that dampens the sudden impact of the hammer, leading to increased energy absorption. However, above 6 wt%, rLDPE-ESP interaction produces a hard/less soft structure that breaks easily upon sudden impact, resulting in smaller amounts of energy absorbed.

4.1.4 Thermal stability

Hanif et al. (2020) study showed that the addition of ESP or CESP fillers to the rHDPE/EVA blend composites improves their thermal stability. According to the author, the fillers decompose in the early stage and produce ash that absorbs heat generated during degradation, thereby delaying the thermal degradation process of the polymer matrix. Increasing the filler loading for both fillers also increased the thermal stability of the blend composites, as the degradation of the ESP or CESP filler constructs a barrier to the gas exhausted from the rHDPE/EVA matrix through heating. Furthermore, the residual mass of each blend composite showed an ascending trend with the addition of filler in the blend composites. CESP filler showed more thermal stability than ESP filler due to its carbonisation process, where the content of CESP filler is mostly carbon or ash, which enables it to withstand high temperatures.

4.2 Water absorption

A study by Farahana et al. (2015a) showed that water absorption increases with increasing ESP filler loading such that higher ESP loading showed more water absorption due to the higher content of filler in the composites. The author proposed that the presence of CaCO₃ in the ESP increased water absorption as the filler increased. The formation of agglomeration of the filler in composites also increases the water absorption due to difficulties in achieving a homogeneous dispersion of filler. Higher ESP loading results in greater water absorption because of increasing voids between ESP fillers and rHDPE/EVA matrices. Furthermore, the presence of the APTES coupling agent improved the interfacial adhesion between rHDPE/EVA matrices and ESP, resulting in lower percentages of water absorption compared to composites without APTES at similar filler loading.

5 CONCLUSION

This study shows the application of eggshells as a filler on recycled polymers. The composites were prepared through melt blending and hot compressed into thin sheets. The eggshell was processed depending on the author and was used in carbonised or uncarbonised form. The study found that the introduction of eggshell powder into composite materials resulted in enhancements in the properties of the composites. The usefulness of compatibilizer and coupling agents was also found to enhance the properties of the composites, especially in their mechanical properties by enhancing the interfacial adhesion between the polymer and the filler. Also, carbonised eggshell powder gave a better result on the properties of the recycled polymers than the uncarbonised eggshell powder.

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