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SYNTHESIS AND STUDY OF THE MECHANICAL PROPERTIES OF BIODEGRADABLE POLYVINYL ALCOHOL/EGGSHELL COMPOSITES

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Abstract

This paper explores the use of eggshell powder (ESP) as a bio-filler material in the biodegradable polymer (polyvinyl alcohol) PVA. ESP is distinguished by a very low density, is abundant, and normally it is disposed of as agricultural waste. This work focuses on the preparation of PVA as a polymer matrix and ESP as reinforcement material by the magnetic stirrer device then investigates the mechanical properties of the produced samples. Various levels of weight fraction of ESP (0.5, 1, and 1.5%), and different particle sizes of ESP (25-75, 75-105, and 105-212 µm) have been studied. Findings reveal that the produced samples with a small size of ESP filler show superior strength in both tension and tear properties and modulus of elasticity as well. The tensile strength and modulus of elasticity increased by 100 and 166%, respectively, with the addition of 0.5 weight % of 25-75 µm ESP. Similarly, the tear strength also increased by 300%. The results reveal the potential of using eggshell wastes can be used to produce value-added biodegradable materials for biological applications and sustainable development.

Keywords: Biodegradable polymer, Composite, Eggshell powder, PVA.

1. Introduction

In light of recent decades in various applications, it is becoming extremely difficult to ignore the existence of problems in the landfills of the used polymers. Therefore, the biodegradable polymer market has been a question of great interest in a wide range of fields. During 2016, the use of biodegradable polymer (polyvinyl alcohol PVA) has been estimated at 172,800 tons. Recent developments in the field of the new technology of renewable natural polymers have led to an interest in polyvinyl alcohol (PVA) which have become highly lucrative due to its biodegradable properties with excellent water solubility. Hence, PVA is used in various applications, such as food packaging, cosmetics, and printing [1-3].

A considerable amount of literature has been published on the uses and importance of PVA. One of these studies produced bio-composite materials for potential medical applications by Balgova [4]. The author produced a set of PVA films at a different weight percent of hydroxyapatite. These films were produced by dissolving the materials in the water at 85°C. After putting the mixture in the mould, it was evaporated at 30°C for 7 days to obtain a thin film (0.5 mm). While Sadhu et al. [5] investigated the mechanical strength of composite samples which contained a PVA material and potato starch. This blend was mixed with nano clay at 1%, 2%, and 3% weight ratios. The mechanical strength showed that the variation with varying compositions. The percent transparency and sealing property of the material have also been studied. Di et al. [6] investigated the evaluation of the mechanical properties of composite PVA/SiO_2. The results showed a significant increase in the mechanical properties of PVA/SiO_2 when compared to PVA. Furthermore, the increased ratio of SiO_2 led to an increase in the damping capacity of the PVA/SiO_2 film. To develop active antioxidant food-packaging membranes, Gaikwad et al. [7] used the PVA matrix which incorporated apple pomace (AP). The results of this research showed that the total phenolic content and antioxidant properties of PVA films enhanced by the incorporation of AP. However, the physical properties, such as tensile strength and elongation at break were significantly lower when the AP content increased. In contrast, the higher AP content led to improve and grow the thermal stability of PVA/AP films.

The recycling of bio waste is very important impact on the environment [8]. Eggshell powder (ESP) was used as a filler in the polyvinyl alcohol (PVA) matrix by Hussein [9]. This polymer composite was produced by mixing PVA with various weight fractions of ESP using a magnetic stirrer. The author observed that the attenuation reduced when the frequency increased up to 40 kHz. At contain a proportion of eggshells 5, 10, 20, 25, 30, and 40%, the transmittance coefficient of the samples improved when the frequency increased up to 40 kHz.

As noticed in the previous study [9], eggshells can be used as a reinforcement particle to produce composite samples. Many advantages lead to the use of the powder of eggshells in producing the composite samples. For example, eggshell (ES) is a biomaterial which contains calcium carbonate in the form of calcites (95% by weight) and organic materials (5%) [10, 11]. Moreover, as eggshells have been proved by many previous studies, they consider one of the worst environmental issues, especially when the industry of egg products is well-developed in some countries due to produce odour and microbial growth. Thus, the effect of eggshell consumption on the environment is a significant factor.

Based on the facts mentioned above, this novel study aims to investigate the usefulness of producing reinforced films made of biomaterials. Polyvinyl alcohol (PVA) is adopted to produce biofilms which strengthened by the eggshells powder. This type of film has various bio-applications, such as coating for tablets, capsules, and dietary supplements. The mechanical properties of produced samples were investigated by using various particle sizes and weight fraction of reinforcing powder material to evaluate the samples and find out the optimum values.

2. Experimental Part

2.1. Materials

The composite films were produced from polymer materials polyvinyl alcohol (PVA) purchased from Central Drug House Company (CDH), India, as a matrix. Table 1 shows the properties of PVA material as provided by the producer. The matrix was reinforced by chicken eggshells powder. Different particle sizes of powder (25-75, 75-105, and 105-212 µm) and different weight fraction (0, 0.5, 1, and 1.5%) used in the experimental investigation to identify the best values of factors which produce the optimum mechanical properties.

Table 1. PVA material properties.

Property	Value
Tensile strength (MPa)	24
Molecular weight	13000-23000
Molecular formula	(CH2CHOH)n
Density (g/cm³)	1.329
Viscosity (cPas)	3.5-4.5
Hydrolysis (mole %)	87-89%
pH (4% water)	4.5-6.5
Loss on drying	5%

2.2. Composite preparation

The aqueous solution of PVA was prepared following the standard of the providing company. In the beginning, 100 ml of distilled water was heated to 80-85°C or just below the boiling point of water. Once the water was heated, the PVA was added lightly into the water with continuous stirring. Waste eggshells were first washed by tap water to remove contaminants. The eggshells were cleaned and washed using distilled water and then dried at 70°C for 4 hours. The pre-treated eggshells were crushed, milled, and sieved the powder by (25-75, 75-105, and 105-212 µm sieve). Eggshells powder was added into the PVA solution stirred with a magnetic stirrer for 1 hr. to produce a highly homogenous solution. Figures 1 and 2 show the eggshells powder (ES) and PVA material used in the current research.

Nine sets of composite samples are produced beside the pure PVA, as shown in Table 2. Mechanical tests applied to these samples.

Fig. 1. Eggshell powder (ES) at different particle sizes.

Fig. 2. PVA material.

Table 2. Sets of produced samples.

System of the composite sample	Materials (matrix and weight fraction of reinforcement)	The particle size of eggshell powder
Sample 1	PVA	-------
Sample 2	PVA + Eggshell powder (0.5%)	(25-75) µm
Sample 3		(75-105) µm
Sample 4		(105-212)µm
Sample 5	PVA + Eggshell powder (1%)	(25-75) µm
Sample 6		(75-105) µm
Sample 7		(105-212)µm
Sample 8	PVA + Eggshell powder (1.5%)	(25-75) µm
Sample 9		(75-105) µm
Sample 10		(105-212)µm

2.3. Mechanical tests

2.3.1. Tensile test

The tensile test has been performed, then a stress-strain curve was plotted for each produced sample, that was compared with the curve of pure PVA. Through these curves, the mechanical properties were determined. These mechanical properties are Young’s modulus, tensile stress, and elongation percentage at the break.

In the current study, ASTM D-638 type IV standard was used to prepare the tensile composite samples. The samples were tested at ambient temperature using a tensile test machine type (LARYEE) at a strain rate (1 mm/min), as illustrated in Fig. 3. The experiments were repeated three times to ensure the results are valid.

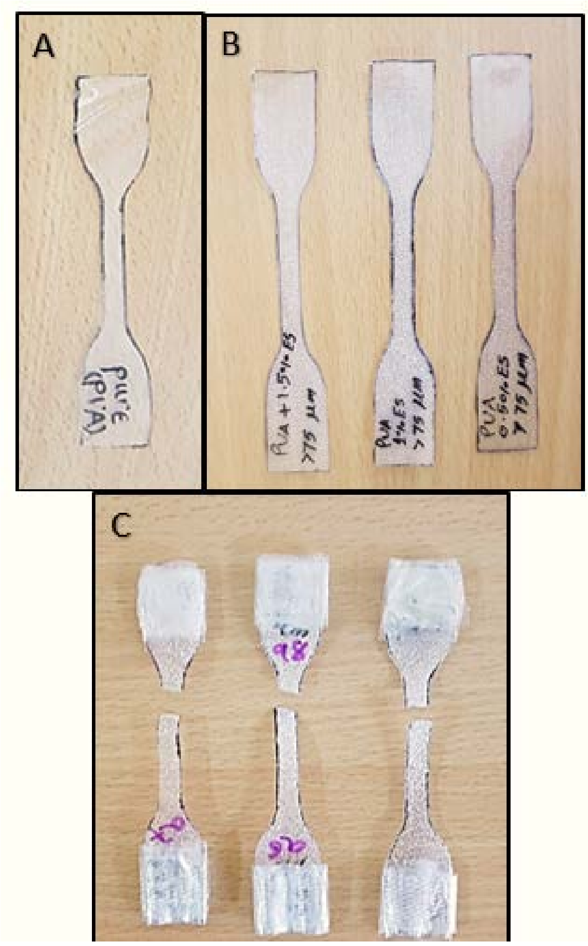

Fig. 3. (A) Pure PVA sample, (B) Composite samples before the test, and (C) Composite samples after the test.

2.3.2. Tear test

A major advantage of the tear test is that it determines the ability of the product to resist the growth of the initial tear. This method is particularly useful in studying the tear of flexible materials, which suffer from a partial rupture intentionally, or otherwise [12].

In the current study, ASTM (D-1938 standard) was used to prepare the tear samples [13]. The samples were tested at ambient temperature using a tensile test machine type (LARYEE) at a strain rate (1 mm/min.). The samples before and after the test are illustrated in Fig. 4. The experiments were repeated three times to ensure the results are valid.

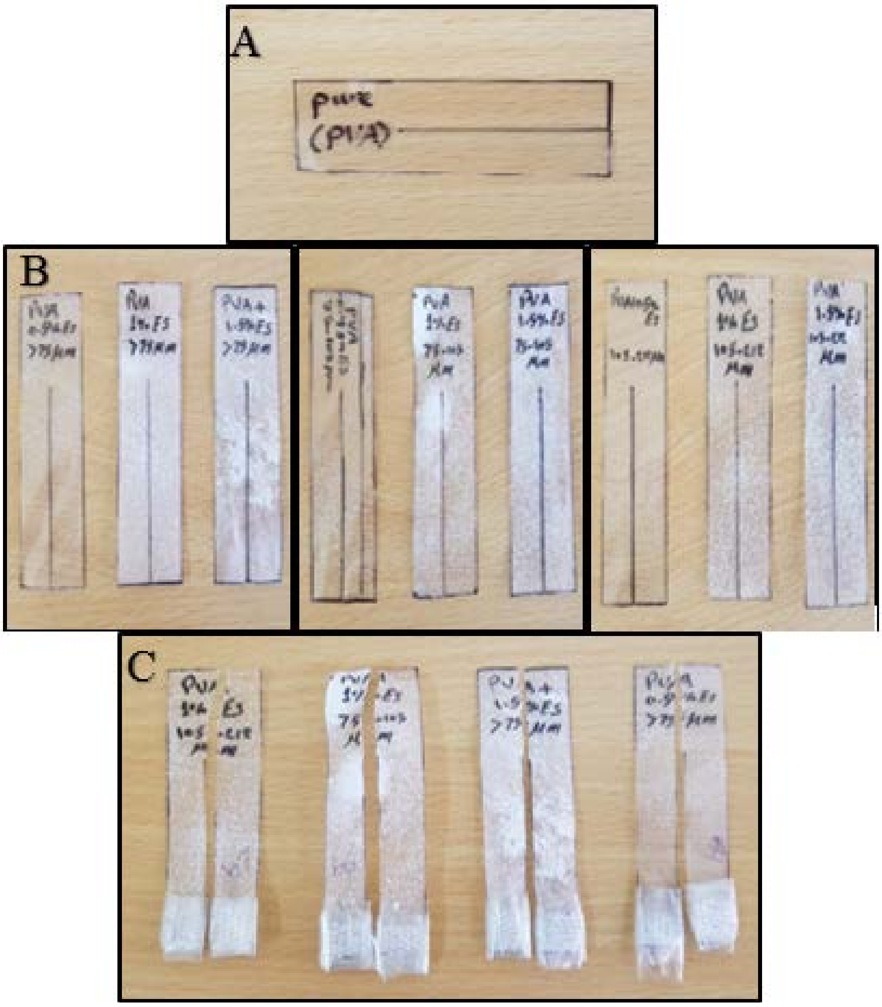

Fig. 4. A) Pure specimen, (B) the samples before the test, and (C) the samples after the test.

3. Results and Discussion

3.1. Tensile test results

The samples, which are produced from pure PVA polymer and after adding the filler (ESP), were tested. Figures 5 and 6 present the effects of ESP weight fraction in PVA on the tensile strength and modulus of elasticity respectively.

From Figs. 5 and 6, it can be seen that reinforcing the pure PVA with ES fillers leads to improve the tensile strength and modulus of elasticity of specimens. Both tensile strength and modulus of elasticity reached a peak at a weight fraction of ESP 0.5% and particle size (25-75 µm). These peaks points, which have the maximum percentages of increasing, tensile strength, and modulus of elasticity, were 100 and 166% respectively. However, the excessive increase of the weight fraction of more than 0.5% leads to a reduction in tensile strength and modulus of elasticity.

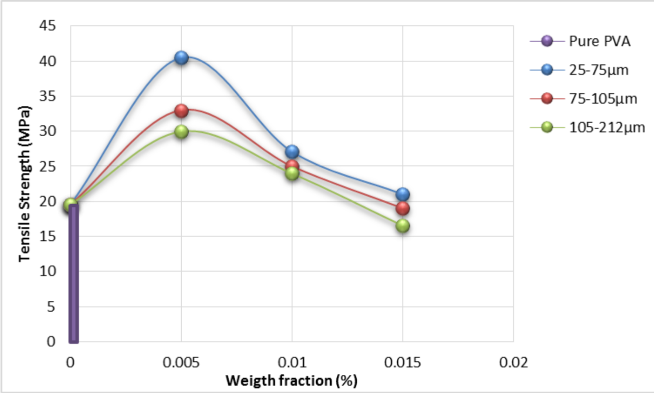

Fig. 5. The relation between tensile strength and weight fraction at various particle sizes of ES.

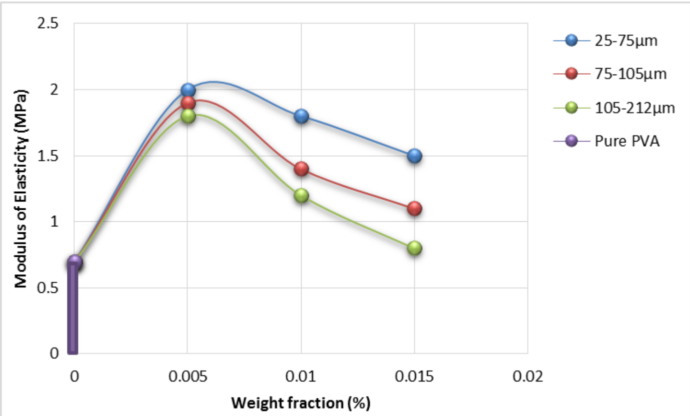

Fig. 6. The relation between modulus of elasticity and weight fraction at various particle sizes of ES.

The most obvious finding to emerge from the analysis is the strengthening mechanism of eggshell reinforcing filler, which means that the amount of these filler particles and the nature of the bonding between the matrix and the filler particles can play an important role. This is a consequence of increasing the amount of filler (ESP) in PVA that leads to an agglomeration of ESP particles in PVA and becomes the bonding weakness and bad wettability between PVA and ESP. Moreover, the movement of the matrix phase is restrained in the vicinity of each particle when the large particles of ESP had been used and therefore the particles bear a fraction of the applied force that transferred from the matrix. Whereas comparing with large particles, the small particle of ESP hinders or impede slipping of matrix chains and requires high stress to bow them in narrow space among particles [14, 15]. These results are in line with those of previous studies.

Figure 7 displays the relationship between the elongation percentage, which calculated at the breakpoint and the weight fraction of the filler particles (ESP) at various particle sizes of filler.

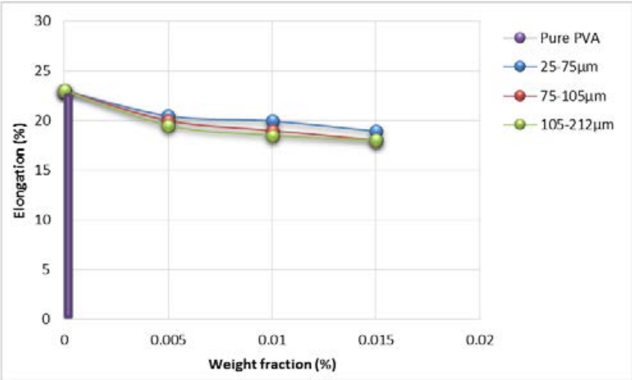

Fig. 7. The relation between the elongation and weight fraction of ESP.

It could be observed from the above figure that the elongation percentage at break decrease with the increase in weight fraction of reinforcing fillers (ESP). This is due to the PVA resin have higher elongation equal to (23%), thus adding ESP in the PVA polymer resulted in the stiffening and hardening of the produced samples. The reduction in resilience and toughness leads to decrement in elongation at break. This finding agrees with a previous study done by Alias and Ismail[16].

3.2. Tear strength test results

Tear strength is dependent on a combination of basic properties such as modulus and tensile strength. Figure 8 shows the relationship between the tear strength and the weight fraction of ESP in the PVA matrix at various particle sizes of ESP.

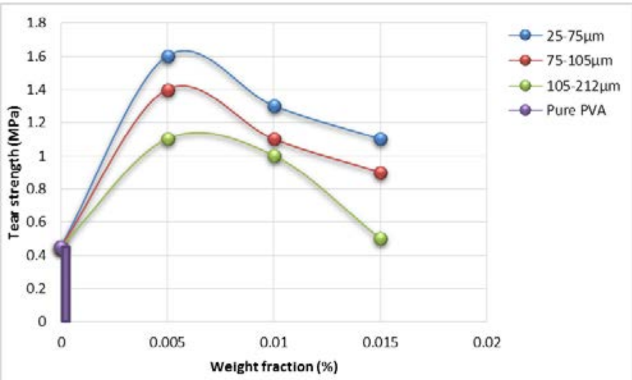

Fig. 8. The relation between tear strength and weight fraction of ESP.

As can be seen from Fig. 8, the use of ESP as a filler in the PVA improves the tear strength of the composite samples to reach its peak (1.6 MPa) when the weight fraction and particle size of ESP are 0.5% and 25-75 µm respectively. After the peak point, the graph shows that there is a gradual decrease in the number of tear strength by increasing both particle size and weight fraction of ESP. Tear resistance of composite samples was dependent on homogenous of particles in the matrix and when increase the amount of ESP in the PVA matrix that caused agglomeration and not good bonding between resin and particles. Hence, tear strength decreased with increasing weight fraction of fillers content in the matrix.

4. Conclusion

The present study was designed to determine the effect of adding the eggshells powder (ESP) in polyvinyl alcohol (PVA) polymer on the mechanical properties. The most obvious finding to emerge from this study is that the mechanical properties of PVA polymer, such as tensile strength, modulus of elasticity, and tear strength were improved by adding the ESP. These mechanical properties reached their peaks at both small particle sizes of ESP (25 -75 µm) and low weight fraction of filler (ESP) in the PVA matrix (0.5%). In contrast, elongation at break of produced samples was reduced through adding the filler (ESP).

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