The formulation and study of the thermal stability and mechanical properties of an acrylic coating using chicken eggshell as a novel bio-filler

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\textbf{A B S T R A C T}

The objective of this study was to evaluate the effect of chicken eggshell (ES) as a bio-filler on the adhesion strength and thermal stability of acrylic coatings. The influence of different particle sizes of ES on the performance of acrylic coatings was compared with commercial calcium carbonate filler by using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and pull-off type equipment. The surface morphologies of the coatings were characterized through field emission scanning electron microscopy (FESEM). The resistance of the coating was also investigated using water immersion and freeze–thaw tests. Morphological studies revealed that the ES filler was well-distributed in the polymer matrix. Furthermore, it was observed that the adhesion strength, thermal properties, water and freeze–thaw resistance of the coating improved with decrease in particle size of ES filler. Overall, the best results were obtained from using ES bio-filler with the smallest particle, although the particle size was bigger than that of commercial calcium carbonate. The improvement in the properties of the coating was attributed to the even distribution of ES particles and better ES/matrix interface.

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\section{1. Introduction}

The effective utilization of chicken eggshell (ES) biowaste is strongly encouraged in our society for environmental and economic reasons. ES which is a byproduct of the aviculture industry has been highlighted recently because of its reclamation potential. Unfortunately, most ES waste is discarded in landfills without further processing. It is known that eggshell waste contains valuable organic and inorganic components which can be utilized in commercial products by creating new value in these waste materials. This study presents a useful bio-filler derived from ES waste and its potential role in the coating industry.

The properties of ES have been extensively studied for various purposes by many researchers. It consists of two materials: the calcified eggshell made of calcite and calcium carbonate crystals and the ES membrane consisting of organic matter. ES contains about 95% calcium carbonate in the form of calcite and 5% organic materials such as type X collagen, sulfated polysaccharides, and other proteins \cite{1-11}. Although there have been several attempts to use ES components for various applications \cite{12-19}, its chemical composition and availability makes ES a potential source of filler for polymer composites. Much attention has been given to the study of bio-filler reinforced bio-polymer composites \cite{20} and its application as coating pigments for ink-jet printing papers \cite{21}. Besides its chemical composition, ES is a potential source of bio-filler for coatings because it is available in bulk quantity, inexpensive, lightweight and environmental friendly.

The major components of coatings are the binder and filler combined with other additives. Several groups have reported the influence of particle morphology, fillers, dispersing agents and nature of the binder material on the performance of coatings \cite{22-28}. The binder forms a continuous phase that provides the main characteristics (e.g. mechanical, chemical) to the coating, while the filler is the discontinuous phase giving additional or improved properties to the coating. The selection of the specific components will affect the general performance of the coating. The compatibility between filler and binder is a key factor to improve the mechanical properties of the coating. Addition of filler decreases the tendency of degradation of the system due to external factors like water ingress \cite{29}.

This paper focuses mainly on the effect of different types of fillers and particle sizes on the thermal stability and mechanical
properties of acrylic coating. Acrylic resin has high heat and impact resistance, as well as good clarity and UV resistance. This polymeric coating system is widely used to provide protective and decorative functions to substrates due to its low cost, good adhesion and more durable resin [30,31]. The application of eggshell calcium carbonate as bio-filler for acrylic resin binder provides an excellent way of recycling eggshell waste. The influence of fillers on the thermal properties, surface morphologies and mechanical properties of coatings is studied by using thermogravimetry analysis (TGA), differential scanning calorimetry (DSC), field emission scanning electron microscopy (FESEM) and pull-off type equipment. This paper also comparatively analyzes the water resistance and freeze–thaw cycle resistance of the coatings.

Clearly, there are limitations of preparing eggshell particle size in this work unless the eggshell is ground to very fine particle size, it will exhibit high aspect ratio due to the thin plate like nature of a shell. Depending on the particle sizing technique this aspect ratio property will strongly influence the assumed particle size, particularly if sedimentation or air classification is used, or indeed if the wrong form factor is applied in light scattering methods. Furthermore, proteins exist which provide some limited elasticity to the shell structure. Therefore, before recommending this novel filler for improved properties the discussion would need extending to consider matrix linkage compatibility between filler and polymer and should explore the role of aspect ratio and filler deformation properties. This will be a subject of future work.

2. Experimental work

2.1. Materials

Chicken eggshells (ES) were used as a bio-filler in this study. The ES membrane was removed and discarded. The ES were then cleaned thoroughly and dried at 90 °C for 12 h in the oven. The dried eggshells were mechanically triturated to a powder form and then milled at a milling speed of 280 rpm for 20 h and 48 h, respectively in a four-roll mill to obtain mean particle sizes of 31.34 μm and 22.99 μm. The Mastersizer Micro Particle Size Analyzer was used to measure the particle sizes and the particle size distribution profiles of the fillers are shown in Fig. 1.

In this research, acrylic resin was used as a binder. Acrylic resin is a 100% solid thermoplastic substance derived from acrylic acid, methacrylic acid, esters of these acids, or acrylonitrile and is a general purpose polymer with good hardness, broad compatibility and good weather-resistance. Acrylic resin in the form of acrylic copolymer (Mn = 60,000) was purchased from Mitsubishi Rayon Co., Ltd (Tokyo, Japan). The components of the coating formulations are listed in Table 1. The acrylic resin was mixed with mineral filler (calcium carbonate) or ES fillers until homogenous using a high-speed disperse mixer. The solvent used for acrylic resin was toluene.

2.2. Film preparation method

The polymer films were prepared by casting the solution on a glass leveled support plate. The solvent was then allowed to

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**Table 1**

Coating formulations: composite name, filler type, filler proportion, particle size and filler surface (BET) area.

<table>
<thead>
<tr>
<th>Composite name</th>
<th>Filler Type</th>
<th>Proportion (% w/w)</th>
<th>Particle size (μm)</th>
<th>BET area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1 = AR-CC</td>
<td>CC</td>
<td>19.00</td>
<td>9.22</td>
<td>10.56</td>
</tr>
<tr>
<td>C2 = AR-ES1</td>
<td>ES</td>
<td>19.00</td>
<td>31.34</td>
<td>87.40</td>
</tr>
<tr>
<td>C3 = AR-ES2</td>
<td>ES</td>
<td>19.00</td>
<td>22.99</td>
<td>148.41</td>
</tr>
</tbody>
</table>

*CC: calcium carbonate.
ES: eggshells.*
evaporate slowly for 5 days at ambient temperature until completely dried. The thickness of the cast films were adjusted using a four sided applicator with the gap sizes ranging from 30 to 300 μm. In this experimental work, the thickness of the dry film was controlled to be in the range of 100–200 μm. The films were easily removed from the glass substrate by immersing the samples in a water bath for 1–30 min. To remove residual water, the films went through another drying process in the vacuum oven for 3 days at a temperature of 40 °C.

2.3. Field emission scanning electron microscopy

Microscopic analyses were carried out using a field emission scanning electron microscope (FESEM) GEMINI® FESEM to examine the surface morphology of the coatings. For FESEM observation, all coating samples were coated in gold and low beam energy of 1 kV was operated to reduce the possibility of any thermal damage to the coatings.

2.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out to observe changes in thermal events in the polymer films using a TGA/SDTA851e model. The films were heated at a heating rate of 20 °C/min under air flow in the temperature range of 30–1000 °C. The weights of samples are 6–10 mg in all cases.

2.5. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to determine the thermal transitions of the polymer films. Samples were heated at a heating rate of 10 °C/min in the temperature range of 30–350 °C under air flow using a Mettler Toledo Star DSC model.

2.6. Static immersion test

Static immersion test is considered as a standard method that evaluates water resistance of films using the gravimetric method. Samples of films were immersed in distilled water at 25 °C. At specific time intervals, the films were removed and were blotted with a piece of paper towel to absorb excess water on the surfaces. Weight change was calculated by Eq. (1) and expressed as a function of time.

\[ E_{sw} = \frac{W_e - W_d}{W_0} \times 100\% \]  

where \( E_{sw} \) is the water uptake ratio of the film, \( W_e \) denotes the weight of the film at different times and \( W_d \) is the dry weight of the film.

2.7. Test of mechanical properties

2.7.1. Adhesion strength

The adhesion strengths of the coated samples were determined by using Instron Micro Tester equipment. The coatings were each sprayed on one side of 50-mm × 50-mm × 2.6-mm steel plates with a film thickness of 0.2 ± 0.05 mm. The coated steel plate was attached to the other bare steel plate (dimensions: 50-mm × 50-mm × 2.6-mm) using epoxy glue (thickness of 0.5 ± 0.05 mm). Then the two steel plates were continually drawn apart in tensile mode at a constant rate of 1 mm/min normal to the bonded surface using the testing device until the coating on the steel plate cracked. Adhesion strength \( f_b \) in MPa was calculated based on following Eq. (2).

\[ f_b = \frac{F}{A} \]  

\( f_b \) is the adhesion strength, MPa; \( F \) is the crack charge, N; \( A \) is the sticking area, mm².

2.7.2. Resistance to freeze–thaw cycle

Each coating was applied to one side of a 50-mm × 50-mm × 2.6-mm primed steel plate at a thickness of 0.2 ± 0.05 mm. The coating samples were placed in a flow of air at 25 °C for 18 h, then frozen in a low temperature freezer at −20 °C for 3 h and finally heated at 50 °C for 3 h in an incubator. The process above is recorded as a freeze–thaw cycle period.

3. Results and discussion

3.1. Characterization of the coatings

3.1.1. Surface micrographs of the coatings

As seen in Fig. 2, the morphology of the ES2 filler is more like ES1 than mineral calcium carbonate. High magnification surface micrographs of the coatings enable the observation of the distribution of the fillers. Both C2 and C3 exhibit a relatively homogeneous distribution of the binder and bio-filler. However, filler distribution was observed to be nonhomogeneous in coating C1. The ES particles were better embedded in the AR matrix than the calcium carbonate particles as shown in Fig. 3. In this study, we did not examine the geometric ratio value of each filler. The geometric ratio value will be a subject of future work. The contributing factor can be attributed to a better ES/matrix interface related to the geometric ratio of the ES particles. A similar geometrical ratio of ES particles (see Fig. 2) could be the relevant factor in obtaining the homogeneity of the AR-ES coatings. Thus, ES particles showed a phase continuity in the AR which was as good as or better than the particles of calcium carbonate [20].

Sample C3 had more even distribution, better ES/matrix interfacial bonding to the steel plate surface and was glossy with a smoother finish compared with sample C1 and C2. The surface structure of C1 was observed to have uneven distribution of the filler which consequently resulted in the formation of a porous structure in the coating compared to C2 and C3. The surface structure of sample C3 indicates that the smallest particle size of ES bio-filler allowed better mixing with the binder which resulted in a more uniform and homogenous coating as observed in its finer micropore structure when compared to C2. The utilization of calcium carbonate from eggshell waste as a low cost coating filler can perhaps be an efficient solution to improve the surface smoothness of coatings while creating new value through bioresource recycling.

The results indicate that the combined elements of acrylic binder and smallest particle size of ES bio-filler have a linear correlation to the better interfacial bonding and uniformity in composition.

3.2. Thermal analysis of the acrylic films

Fig. 4 shows that the TGA curves of the acrylic films were similar. According to these results, degradation of the films occurred in two steps (at around 300 and 800 °C), whereas the thermal degradation of the films left a thermally stable char at 900 °C. The total weight losses of samples C1, C2 and C3 were about 79%, 82% and 80%, respectively. Results show that when the particle size of the filler in the acrylic film decreases, the total weight loss of the film also decreases and at the same time the temperature range of the degradation process becomes narrow (C2 = 120.2 °C, C3 = 109.1 °C and C1 = 87.6 °C). Weight loss in the second step which occurred at around 800 °C was due to the formation of calcium oxide (CaO) and the release of carbon dioxide (CO₂) by the following reaction:

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]  

(3)
In the second step, all the samples had nearly the same amount of weight loss in the range of 14.5–15.7% with less than 8% difference between the samples. This indicates that the acrylic films contained the same amount of filler. Sample C3 had the least weight loss (14.5%) when compared to samples C2 (15.4%) and C1 (15.7%). This may be attributed to the degradation process of C3 having the narrowest temperature range in the second step. At the end of the second step weight loss, the residual thermally stable char contained CaO which was stable over 900 °C. The residual weight of sample C3 was higher than C2 due to the smaller mean particle size and higher surface area of ES2 resulting in an enhancement of the thermal stability of the acrylic film. The relatively higher surface area of the particles enabled a strong interaction on the thermal stability due to Van der Waals attractive force and mechanical network between the ES filler and matrix during degradation [32–35], albeit the low filler content. However, the residual weights of samples C3 and C2 were lower than C1. This situation may be due to the presence of impurities in the ES filler which decomposed at the first step in the temperature range of 280–380 °C and lower CaCO3 content compared to commercial CaCO3. The exact degradation
3.3. Differential scanning calorimetric analysis of the acrylic films

The DSC curves of the acrylic films exhibited endothermic peaks under air flow in the temperature range of 30–350 °C. When the acrylic films were heated, the two melting peaks with decomposition of the metastable and stable modification took place over a broader range of temperatures for each sample, as in Fig. 5. The area under the curve can be used as a measure of the degree of crystallinity in the sample, provided we can somehow get a value of the specific enthalpy of fusion. During the thermal decomposition of the acrylic films, heat was absorbed due to the melting with decomposition of acrylic copolymer to acrylic monomers [36,37]. The melting peaks of the metastable modification of acrylic films C1, C2 and C3 were observed at about 269, 278 and 280 °C, respectively. At the same time, the stable modification crystallizes from the resulting melt (endothermic peak followed by an exothermic peak). The stable modification melts afterwards at about 291, 295 and 297 °C, respectively [38].

The results suggest that adding the same proportions of different types of fillers or particle sizes have influenced the melting points of the acrylic films. This was attributed to the increase in interstitials volume or the increase in ES/matrix surface contact [39]. These results seem to show a positive correlation between the BET area and melting point: the higher the BET area of the filler, the higher the melting point of the acrylic film. This situation may also be related to the strong interaction between the ES filler and the acrylic binder in terms of surface charge and chemistry, but also very critically on the size and shape of the particles on the rheology of a polymer melt [40].

To determine the total enthalpy of all probable reactions in the present study, the area under the entire endotherm curve was integrated and the results were determined. The enthalpy of samples C1, C2 and C3 were 257.92, 338.49 and 460.81 (J/g), respectively. Results show that the higher the enthalpy of the sample, the higher the overall heat energy required for melting. This situation may be related to the Van der Waals attractive force and mechanical network between the filler and binder [34,35]. This means that the higher change in enthalpy under endothermic decomposition is because of the higher amount of heat absorbed during chemical and physical reaction. The area under the DSC curves also indicated that samples C2 and C3 had higher degree of crystallinity than sample C1 which was made using mineral calcium carbonate filler [41,42].

3.4. Static immersion test

The water uptake versus time curves of the acrylic thin films is shown in Fig. 6. It was observed that the water uptake of the film decreased with the decrease in the particle size of ES filler used. The maximum water uptake of C3 was 0.23%, while the water uptake of C2 and C1 was 0.64% and 0.67%, respectively. The even distribution of the smaller ES particles resulted in a uniform and smoother surface structure, thereby improving impermeability and enhancing the water resistance of the thin film. Molecules of water did not permeate C3 easily, which led to the lowest water uptake after the immersion test. The weight of all the thin films increased less than 0.7% after the water immersion test, which indicates that the overall water resistance of the coating formulations was very good.

3.5. Mechanical properties

3.5.1. Adhesion strength

Table 2 displays the average adhesion strength of the coating samples added with different types of filler. Sample C3 had
the highest adhesion strength of 1.68 MPa compared with C2 and C1 which had values of 1.42 MPa and 1.26 MPa, respectively. An increase in the adhesion strength of the AR–ES coating was observed when the smaller particle size of ES filler was used. The adhesion strength of the AR–ES coatings was higher than that of the AR–CC coating even though both the ES fillers had larger particle size than the commercial calcium carbonate. The improvement in the mechanical properties can be attributed to a better ES(matrix) interface related to the geometric ratio of the ES particles. In fact, ES particles were better embedded in the AR matrix than the calcium carbonate particles as shown in Fig. 3. In conclusion, ES obtained from aviculture waste can easily be used as a filler for acrylic resin, which provide better reinforcement properties [20].

3.5.2. Freeze–thaw resistance test

Figs. 7 and 8 show sample coatings C1, C2 and C3 applied on the steel plate surface before and after cyclic freeze–thaw testing. The coatings were examined visually for cracks, coagulated particles, blisters and color changes. After 70 freeze–thaw cycles, C1 showed some small blisters and color change on the coating surface whereas C2 and C3 had less blisters and only slight color change. However, all sample coatings did not detach from the substrate and were free from cracks and coagulated particles.

4. Conclusions

Sample C3 had higher adhesion strength than C1 and C2. Coating C3 (ES2) first step was better than that of the calcium carbonate filler. However, the final residual weight of C2 and C3 was lower than C1 due to the impurity content in the ES. In conclusion, eggshells obtained from aviculture waste can easily be used as a biofiller for acrylic coatings with better water resistance, mechanical and thermal properties as well as resistance to freeze–thaw cycles compared with coatings made using commercial calcium carbonate filler.

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References