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Characterization and Morphological Analysis of Organic Calcium Carbonate Filled Polypropylene

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Abstract. The environmental issues caused by the usage of petroleum-based plastics have become a major concern these days. The depletion of the source is also being put into consideration for the use of the polymeric material. Besides improving the polymer properties, the use of waste substances will reduce environmental pollution. For this study, the $CaCO_3$ was derived from waste eggshell and used as fillers in a polypropylene matrix. The eggshell was subjected to grinding to obtain the powder form, the commercial form of $CaCO_3$. The compound was molded using the hot press machine after being mixed in an internal mixer. The samples were subjected to several characterizations and testing such as Fourier Transformation Infrared (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Tensile test. The effects of filler size of 20µm, 50µm, and 100µm at 30 wt.% eggshell powder contents on morphological and other properties were studied. The FTIR and XRD analysis identified the reaction between the filler and matrix. The tensile strength decreases with a decrease in particle size of the composites. The filler morphology and fractured surface of the composite were studied using SEM and determined to have well-dispersed particles with fibrillated fracture surface for 100 µm and 50 µm while 20 µm have a smooth surface.

INTRODUCTION

Polymer composite comprises of two or more components that are the mixtures of polymers with organic or inorganic additives. The additives are either continuous or discontinuous based on their geometries. The continuous usually have fiber or ribbons shaped additives. On the other hand, the discontinuous, also known as short fiber usually shaped in flakes, platelets, spheres, or irregulars. Additives for polymer composite can be classified as reinforcements, fillers, or reinforcing fillers based on their main purpose for the addition in the composite. Up to 70% of fiber can be added for continuous composite. Meanwhile, the discontinuous type can only be filled with less than 30-40% of the particle.

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Polymers are receiving huge attention and demand these past years due to their properties and convenience. Polymers are often available in daily life for packaging, stationery, electronic devices, and many more. These applications show that plastic industries are increasing in demand. Polypropylene (PP) is one of the most promising candidates in the field of thermoplastics. It is currently used in the automotive and the packaging industry and the second most used polymer after Low-Density Polyethylene (LDPE). PP is preferable because it has the lowest density compared to other commodity plastics, excellent thermal stability, flexibility in design, and simplicity in recycling [1]. Although the main use of PP is in an automotive application, its other applications are to be explored because of its excellent potential properties. Unfortunately, PP is still not a choice in other applications due to its inability to exhibit superior properties compared to other polymers available. It is reported to have low modulus, high notch sensitivity, and poor impact resistance, limiting the use of PP as engineering thermoplastic. Therefore, the improvement of these characteristics of PP has been an important and urgent task to extend the possible varieties of PP applications. PP is often used as a composite by including fillers or reinforcement to alter its crystalline structure and morphology [2].

To enhance the property of PP, research uses a variety of fillers. One of the examples is the eggshell powder. Egg processing industries such as egg farmers, chick hatcheries, and egg breaking plants generate many eggshell waste [3,4]. In the United States, eggshell waste is ranked 15th on the Environmental Protection Agency's (EPA) list of food sectors that pollute the environment [5]. Eggshells compensate for about 9–12 percent of overall egg weight, and when it refers to the chemical composition of an eggshell, 98% is made up of dry matter and 2% is made up of water. The dry matter is mainly made up of crude protein (5%) and ash (93%) [6]. Thus, a lot of research has been done to use eggshell as a potential candidate to replace the mineral calcium carbonate as filler in the polymer. Bashir & Manusamy (2015) have experimentally evaluated the characteristics of eggshell powder and revealed that it is similar to the commercial calcium carbonate, which makes it applicable for potential source of filler [7]. Moreover, Dhaliwal & Kapur (2013) [8] have stated that the performance of the composite has been increased using the modified eggshell powder rather than the conventionally used $CaCO_3$. Therefore, this study seeks to investigate the waste eggshell as filler in the propylene matrix and the effect of the particles size on the properties of the polymer matrix composite.

MATERIALS AND METHODS

Materials

Polypropylene (PP) having a density of 0.90 gcm^{-3} and melt flow index (MFI) of 10.5 g/ 10 min at 230˚C acquired from Lotte Chemicals Titan. Eggshells were collected at the cafeteria around International Islamic University Malaysia.

Methods

First, the eggshell membrane was thoroughly removed from the eggshell. Next, the eggshell was dried for 24 h prior to grinding into powder form. Then, the eggshell powder was sieved into different particle sized. Next, eggshell powder was mixed with the polypropylene using an internal mixer at 190˚C with processing torque of 50 rpm for 8 minutes. Then the mixes were hot pressed at 190˚C for 5 minutes. FTIR was done on the organic $CaCO_3$ (OCC) powder and the composites to by using FTIR Spectrum RX1 Perkin Elmer analyzer in 4000-400 cm^{-1} wavelength with 32 scans. tensile fractured surface of the composites was subjected to the (SEM) (Philips XL-30 W/TMP) with an operating voltage of 9 kV to investigate the surface morphology. The tensile test was conducted using Shimadzu Universal Testing Machine according to ASTM D 638 and specimen type-IV. The crosshead speed was set to 5mm/min. The composites were formulated as in Table 1.

TABLE 1. Body formulation of polymer composites prepared with filler of different particle size

Composite Name	Filler Particle Size (μm)	Proportion of Filler (wt.%)
PPOCC20	≤20	30
PPOCC50	≤50	30
PPOCC100	≤100	30

RESULTS AND DISCUSSION

The fractured surface of the tensile test samples that was observed using SEM are shown in Figure 1. From Figure 1 (a) the tensile fractured surface of the PP is smooth. Bootklad & Kaewtatip (2013) [9] have suggested that the fractured surface of PP is smooth due to the easy crack propagation, which is like a typical brittle fracture. In contrast, the fibrillated matrix pulled out in Figure 1 (b) and (c) indicated ductile fracture of the composites. The voids surrounding the filler indicate the weak adhesion between the filler and matrix. However, the filler with a smaller size shows finer embedment in the matrix with smaller voids surrounding the filler. Figure 1 (d) shows that there is the least void in the PPOCC20 sample. The fracture surface of PPOCC20 was also smooth with the finely distributed particles and the empty hole where the particle debonding is observed.

However, SEM images of all composite sample show particle dislocation from its original place, leaving a void in the matrix, indicating that the bonding between the matrix and filler is not too strong. This agrees well with the observation of Hassen et al. (2015) [10] in which they proposed that the incorporation of large particles caused the formation of voids. They have suggested that the properties of PP, which has very low surface energy and surface tension, cause de-wetting of those particles, which permits the debonding of OCC particles in the PP matrix. The decrease in tensile strength is associated with large cavities and cavitation of the particles. Theoretically, the smaller particle will have the highest tensile strength due to the higher surface area in contact with the matrix. The stress initiation also can build up the local stress due to the inhomogeneous particle size distribution. This is because the particles were assorted with a range of sizes, therefore, variation between each particle can be expected.

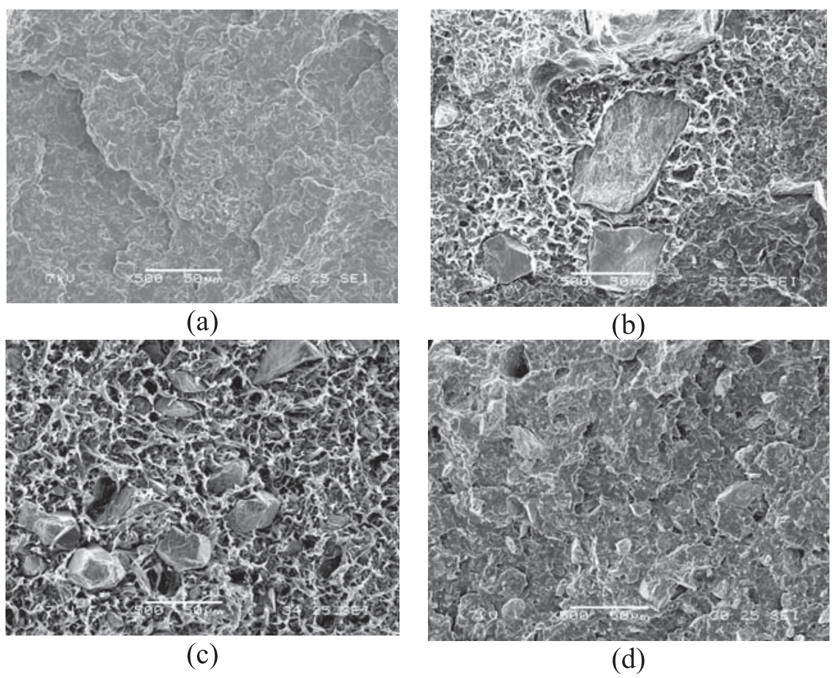

FIGURE 1. Tensile fractured surface of a) PP, b) PPOCC100, c) PPOCC50 and d) PPOCC100 at 500X magnification

XRD was conducted to investigate the crystalline phase of the OCC. Figure 2 shows that the major crystalline phase of eggshell is of calcite ($CaCO_3$). This result agrees with most of the researches done by other researchers which have also found that raw eggshell composed of high percentage of $CaCO_3$ [11]. The characteristic peaks showed by the OCC match the characteristic peaks of calcite at 2θ, which are 29.442˚, 36.021˚, 39.506˚ and 43.195˚ [12]. The highest intensity can be observed at 2θ= 29.442. This result agrees with the observation of Betancourt & Cree (2017) [13] that calcite has a very sharp peak at around 30˚. The peaks shown in XRD pattern show the characteristic peaks of calcite and indicate the high purity of particles [14]. The XRD of composites shows the separate phase of the matrix and filler which can be observed for the peaks of PPOCC100, PPOCC50 and PPOCC20, the diffraction angle of PP can be seen at 14.21˚, 17.12˚, 18.82˚, 21.25˚ and 22.12˚ while the rest represent the peaks of the calcium carbonate, as has been discussed earlier. This shows that the solid phase of the matrix and filler can be distinguished by using

XRD. The composites show the same XRD peak at 2θ for every particle size.

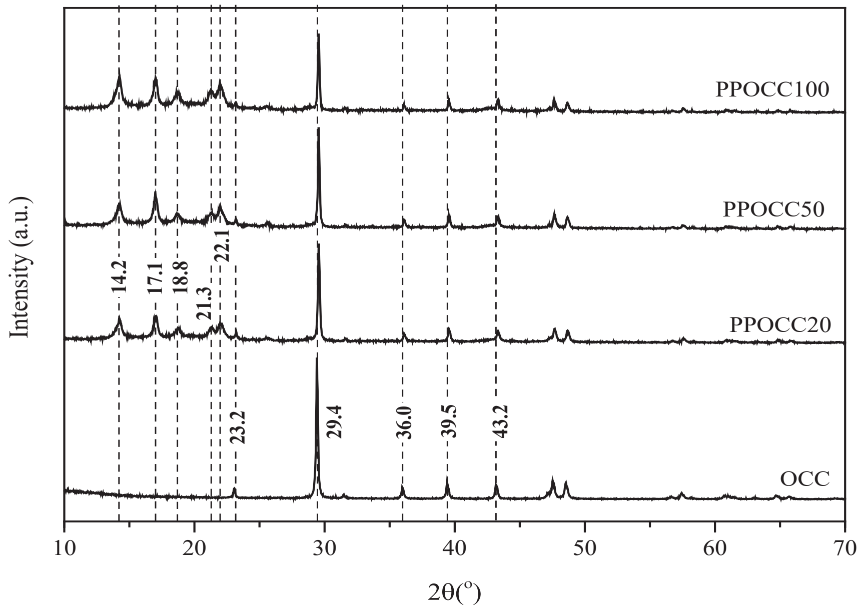

FIGURE 2. XRD pattern of OCC and PPOCC

Figure 3 shows the FTIR spectra of OCC and the composites. From the figure, the vibration band of the OCC is found to be similar to the commercial calcium carbonate. It shows three active bands of carbonate ion at 1413, 874, and 712 cm^{-1}, which relates to the v_3 antisymmetric stretching, v_2 out-of-plane bend, and v_4 in-plane bend, respectively. Meanwhile, the bands at 2951, 2918, and 2836 cm^{-1} belongs to the C-H stretch of the PP and the peaks at 1447 and 1374 cm^{-1} shows the CH_2 bend and CH_3 bend of PP [14]. Moreover, FTIR spectra of PPOCC100, PPOCC50 and PPOCC20 show the presence of all peaks from the raw PP and OCC and the absence of new peaks in the composites. This shows that there is no chemical bonding between the matrix and filler. The dissimilar nature between PP and OCC causes the bonding to occur by surface compatibility or closure between the polymer matrix and filler particles [15].

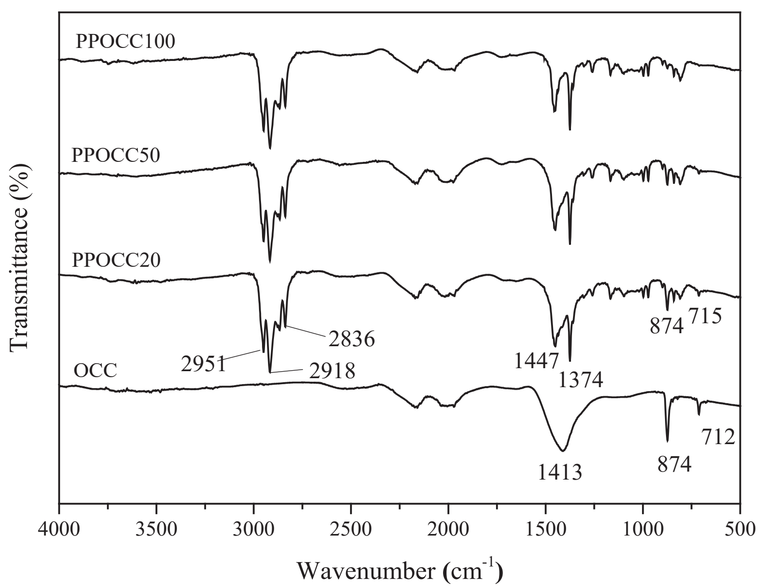

FIGURE 3. FTIR spectra of OCC and PPOCC composites

The tensile strength of the composites seems to be lower as the particle size decrease, which in this term disagree with the finding of previous research by [13,16]. From this study, the highest tensile strength is shown by PP followed by PPOCC100, PPOCC50, and PPOCC20 with 35.2 MPa, 30.7 MPa, 30.1 MPa and 29.9 MPa, respectively. After a thorough check on the method and literature, it is concluded that such a result was affected by the molecular weight of the matrix [17]. It is known that thermoplastic will experience a decrease in molecular weight when subjected to heat. The composites were all subjected to high temperature during the mixing process and hot pressing instead of only hot pressing for PP without filler. The low tensile strength also might be caused by the inhomogeneity of the particle size thus affecting its distribution in the matrix, which initiates local stress for deformation [10]. The non-uniform dispersion and formation of stress concentration points causes the tensile strength to deteriorate [18]. This finding supports the hypothesis that smaller particles can be integrated in greater amounts than larger particles and have more stability in the composite, probably through nonpolar–nonpolar contact with the PP matrix, and that after a certain limit, the filler particles will be agglomerated (or phased out) within composite [19].

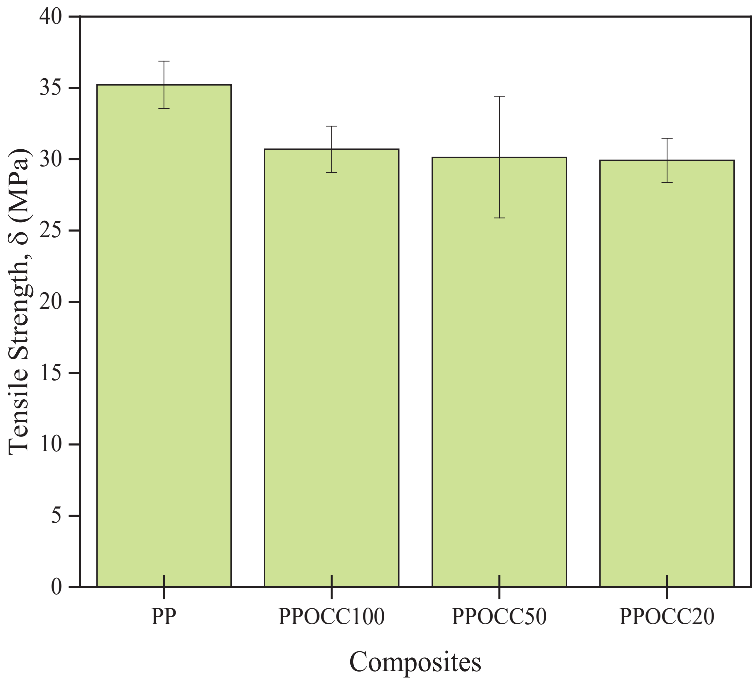

FIGURE 4. Tensile strength of PP and PPOCC composite

CONCLUSION

In conclusion, the SEM images show the morphology of the composite with evenly dispersed particles of eggshell filler. Tensile strength shows that the composite PPOCC100 has the highest tensile strength of 30.7 MPa followed by PPOCC50 with 30.1 MPa, and PPOCC20 with 29.9 MPa. Moreover, the FTIR and XRD show the compatibility between matrix and filler while clearly distinguishing characteristics of the peaks between both filler and matrix. Therefore, it can be summarized that the calcium carbonate can be derived from eggshell and acts as filler in polymer composite which shows great potential for future utilization. Besides, this study also proposed that the effect of particle size is quite significant to the mechanical properties of the composites.

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