

Polymer Composites Fabricated with Calcium Carbonate Recovered from Acid Mine Drainage of the Witwatersrand Eastern Basin

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An environmentally benign hydrothermal urea hydrolysis method for treating acid mine drainage has been developed, enabling the recovery of the aragonite polymorph of calcium carbonate from the three basins in the Witwatersrand region (Gauteng, South Africa). Of the three basins investigated, the calcium carbonate recovered from the Eastern basin displayed the highest crystallinity and average aspect ratio when compared to the other basins. This made it an interesting candidate for the preparation of polymer composites. In this preliminary study, the aragonite particles recovered from the Eastern basin acid mine drainage (with and without the suspended solids) were incorporated at 5 wt.% into an ethylene propylene copolymer via melt compounding. The resulting composites were then investigated for their morphologies, thermal and mechanical properties to establish the influence of particles on the polymer matrix. The results showed that the particles had a heterogeneous nucleating effect on the polymer matrix. The particles imparted an improved balance of toughness and stiffness to the ethylene propylene copolymer. The study demonstrated the possible industrial utility of the calcium carbonate recovered from the acid mine drainage, thus the self-sustaining viability of the treatment method.

1. Introduction

Particulate fillers in polymers have been used for a variety of reasons ranging from cost reduction to functional fillers, tailoring the matrix for specific performances (Rothon & DeArmitt, 2017). That is, the final performance of the polymer composite (e.g. optical, thermal, mechanical properties, etc.) is governed by the filler's chemical composition, particle size, shape and surface characteristics, concentration as well as its dispersion in the polymer matrix (Liang, 2013). The filler also has a significant impact on the polymer composite's processing parameters such as viscosity, heat transfer, etc. (Mallick, 2018). On the other hand, polypropylene (PP) has seen tremendous growth in demanding applications especially where light weighting and high strength are required, like automotive applications and others. This has continued to stimulate research in developing PP composites in search of novel properties (Murariu et al., 2023). Calcium carbonate (CaCO₃) has been extensively used as a discontinuous phase in the polypropylene (PP) matrix, with the resulting composites showing a variety of enhanced properties, such as improved impact strength (Chafidz et al., 2016), fracture toughness (Afshar et al., 2010), and elastic modulus (Eiras & Pessan, 2009), to name but a few. Property enhancements have been shown to be facilitated by the method of composite preparation such as the treatment of the CaCO₃ particle surface (Li & Dou, 2011); processing technique (Faud et al., 2010) and the level of dispersion of the particles (Zhu et al., 2014), in the polymer matrix. These factors are critical as composite preparation is a balancing act where one or more matrix properties can be degraded while improving on another (Ezenkwa et al., 2021). The bulk of the reported literature on PP/CaCO₃ composites are based on ground and/or precipitated CaCO₃,

predominantly the calcite polymorph (Thenepalli et al., 2015). However, in this work we focused on the aragonite polymorph of the mineral, and not only because of its unique morphology (high aspect ratio) and highest density when compared to the other polymorphs. This was mainly due to a method developed to recover aragonite from the acid mine drainage (AMD) of the three goldfields of the Witwatersrand basin (Gauteng, South Africa), using an environmentally benign synthesis method. The preliminary study demonstrated that of the three basins evaluated, the Eastern basin AMD gave the particles with the highest aspect ratio, and these particles were selected to evaluate the utility of the recovered mineral in polymer composite applications (Khumalo et al., submitted). The use of aragonite for PP reinforcement has been reported where it imparted better composite performance when compared to conventional calcite (Jing et al., 2018a). However, PP reinforced with aragonite recovered from AMD has not been published and this is endeavored here.

In this study, we present the results of ethylene polypropylene composites prepared using two aragonite samples recovered from the Eastern basin mine wastewater under slightly different method conditions. That is, one method (proprietary), which involves the pretreatment of the AMD to determine if this would have an impact on the morphology and purity of the resulting particles while the other method does not, the AMD was reacted as received (Khumalo & Chirwa, 2024).

2. Experimental

2.1 Materials

A natural ethylene propylene copolymer (*Safron*®C765-15NA), a commercial product (Safrisol Pty Ltd, South Africa) with a melt flow rate 15 g/10min (230 °C/2.16 kg) and density 0.9 g/cm³ was supplied and used to prepare the composites. The analytical reagents, calcium stearate (CaSt) and urea, were purchased from Sigma-Aldrich South Africa. The AMD was collected in Springs (EB) from the shaft pump before it enters the treatment plant. The aragonite samples were recovered using the highest urea-to-metal ratio (concentration) using a previously reported method (Khumalo & Chirwa, 2024). The main difference was that for one sample (Eastern basin no-sludge – EBNS), the AMD was pretreated using a proprietary method to remove the suspended solids before the reaction, while the other sample (Eastern basin with-sludge – EBWS) was reacted without any pretreatment. The recovery reactions were performed in triplicate.

2.2 Composite preparation

The composites were premixed as 500 g batches and dried overnight in an oven at 60 °C prior to melt mixing (see Table 1 for compositions). The CaCO₃ was loaded at 5 wt.% in the composites, firstly to evaluate the effect of the filler as a preliminary study. Secondly, in another study, this level of loading was reported to give the highest tensile and flexural strength values of the composites (Jing et al., 2018a). The control sample was subjected to the same processing as the PP/CaCO₃ composites. The samples were extruded using a Ninjing Giant A SHJ-20 co-rotating twin screw (China), screw L/D ratio of 40. A screw speed of 20 rpm was used with a temperature profile starting at 140 °C in the feeder zone, going up to 180 °C at the die. The resulting extrudates, were granulated and dried in the oven at 60 °C overnight prior to injection moulding for tensile test specimen preparation. The test specimens were injection moulded using a TMC-30H injection moulding machine (China) with a temperature profile between 190 and 240 °C, and a mould temperature between 50 and 60 °C.

Table 1: Composite formulations

Sample	PP (wt.%)	CaSt (wt.%)	CaCO ₃ (wt.%)
PP	99.7	0.3	0
PP-EBNS	94.7	0.3	5
PP-EBWS	94.7	0.3	5

2.3 Sample characterization

The morphologies of the obtained precipitates and the fractured surfaces of the composites were determined using images taken on a Joel JSM-IT100 InTouchScope™ Scanning Electron Microscope (SEM) (Japan) at different magnifications. The elemental mapping of the composites' fractured surfaces was performed on the Thermo Fischer Scientific energy dispersive X-Ray (EDS) (United States). The crystalline phase determinations of the composites were measured on the PANalytical Aeris Research XRD system (United Kingdom), using Cobalt radiation at 36 kV/36 mA. The melting and crystallization properties of the composites were measured on the TA Instruments Q2000 differential scanning calorimeter (DSC) (United States) after removing their thermal history using a heating and cooling rate of 10 °C/min under nitrogen atmosphere. The decomposition

profiles of the composites were measured using a TA Instruments thermogravimetric analyzer (TGA) Q5500 (United States) at a heating rate of 10 °C/min under nitrogen atmosphere from ambient temperature to 700 °C. The flexural modulus and impact properties of the composites were determined according to ISO 178 and ISO 179 standard test methods, respectively.

3. Results and discussion

3.1 Morphology and thermal properties

The images of the precipitates, EBNS and EBWS are shown in Figure 1. The dimensions of the particles were measured using the image analysis software, Image J2, where ten particles were measured from a minimum of two different SEM images of each sample (Rueden et al., 2017). The samples were found to have slightly different aspect ratios with the EBNS being higher on average than that of EBWS, 8.7 vs. 7.2, respectively. The EBNS sample was characterized by uniform thin particles while the EBWS sample had wide range of particle thickness and some irregular/spherical particles (Figure 1b).

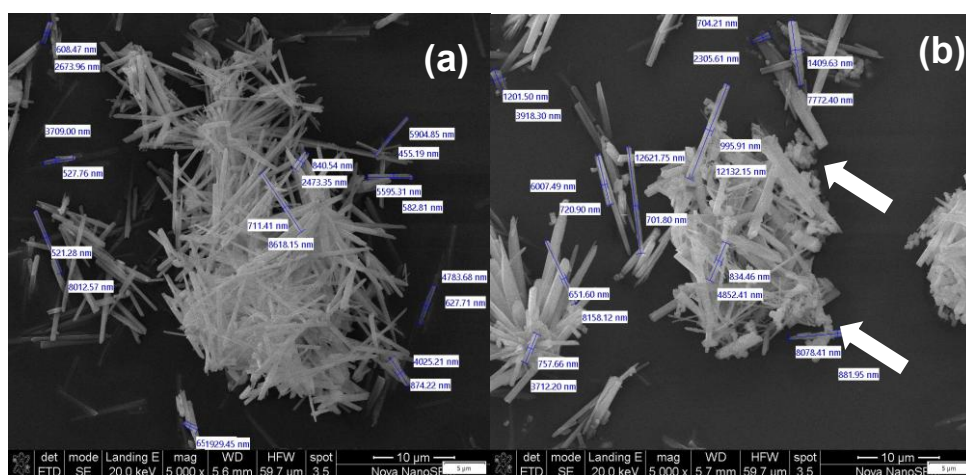


Figure 1: SEM images of the particles recovered from the Eastern basin AMD (a) EBNS and (b) EBWS

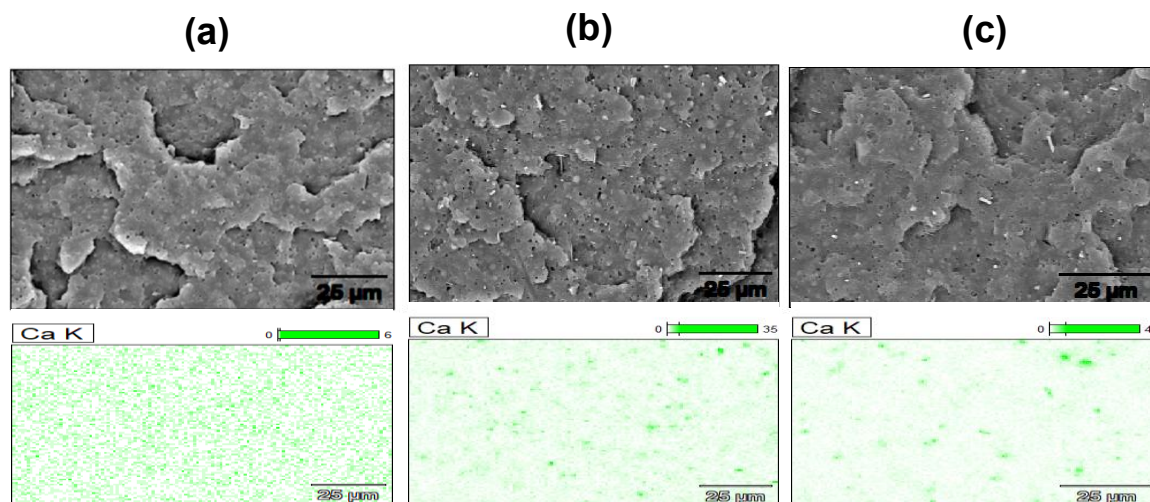


Figure 2: SEM images of the composites fractured surfaces and elemental mapping for calcium (a) PP, (b) PP-EBNS, and (c) PP-EBWS

The observed differences could be attributed to the pretreatment of the EB AMD where the other constituents (e.g. sulphate ions, ferric ions, etc.) were systematically removed for the EBNS sample, while the EBWS sample would contain other precipitates than aragonite. The particle purity is a subject of an ongoing investigation. The presence of sulphate and other ions has been shown to inhibit and/or retard the growth of CaCO_3 crystals (Goetschl et al., 2019). The spherical particles observed in the EBWS sample have been reported previously

when urea hydrolysis was used to treat AMD, as amorphous and low crystalline minerals of iron (Subrt et al., 2011). The images of the composites' fractured surfaces are shown in Figure 2. The calcium detected in the neat sample (Figure 2a) was from the calcium stearate used in all composites. The composites are characterized by uniformly dispersed aragonite particles as shown by the darker green spots for PP-EBNS and PP-EBWS mapping (Figure 2b and 2c), respectively confirming the effectiveness of the composite preparation method. The XRD reflection patterns of the composites are presented in Figure 3. The composites displayed similar reflection patterns as the neat polymer, all dominated by the α -crystalline form of polypropylene with Miller indices (110), (040), (130), (111), (131) and (060). The presence of small amounts of the β -crystalline form could not be completely ruled out as its indices, (300), (301) and (041), overlap with those of the α -crystalline form as shown (Lanyi et al., 2020). The results indicated that the incorporation of aragonite did not have an influence on the matrix crystalline phase.

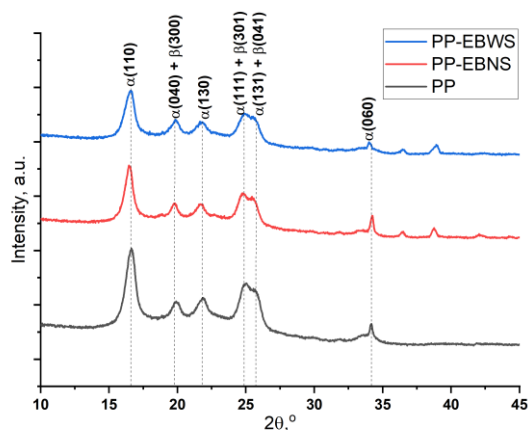


Figure 3: XRD reflection patterns of the composites

The overlay of the DSC crystallization curves is shown in Figure 4a. The aragonite had a heterogeneous nucleating effect on the PP matrix as shown by slightly higher crystallization peaks of PP-EBNS and PP-EBWS when compared to that of neat PP (121.4 and 122.1 °C vs. 120.8 °C, respectively). The EBWS displayed a slightly better nucleation performance compared to EBNS, this was proposed to be due to the wide range of particle sizes as observed from the SEM images of the particles (Figure 1).

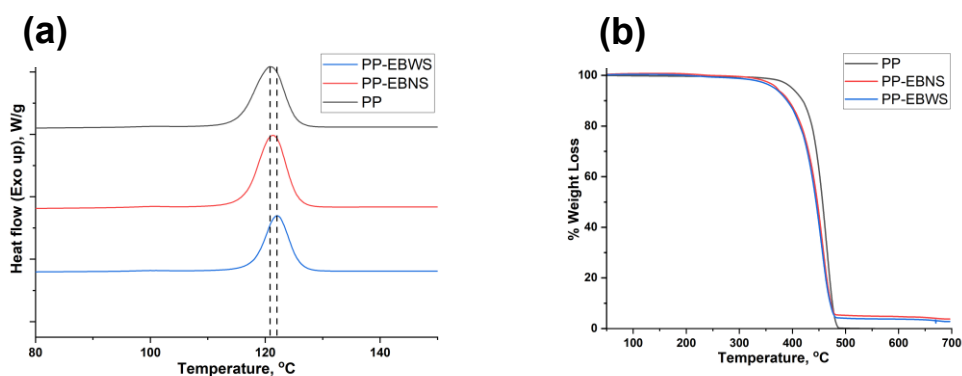


Figure 4: Overlay of the (a) DSC crystallization curves, and (b) TGA decomposition profiles of the composites

The decomposition profiles of the samples are shown in Figure 4b. The incorporation of the aragonite particles recovered from the AMD had a negative impact on the thermal stability of the PP matrix. The composites' onset temperature of decomposition was found to be 368 °C when compared to 394 °C for the neat PP. The negative impact of CaCO_3 on PP thermal stability reported previously was attributed to poor dispersion of the filler and poor interaction with the matrix (Jing et al., 2018b). In this study, it could be attributed to the presence of other metallic impurities precipitated with the aragonite from the mine wastewaters. This could be countered by incorporating some metal deactivating additives that form stable complexes with the impurities, thus rendering them unreactive with the matrix (Fitroni et al., 2016). However, that is beyond the scope of this work.

3.2 Mechanical properties

The mechanical properties of the composites are shown in Figure 5. The composites displayed a slight decrease on the impact strength (toughness), when compared to the virgin material (Figure 5a). The PP-EBNS sample displayed a 12 % decrease while the PP-EBWS sample only decreased 3 %. This was attributed to poor interfacial interaction between the matrix and CaCO_3 particles since their surfaces were not individually treated with a surfactant (Moczo & Pukanszky, 2019). At 5 wt.% loading, the aragonite increased the flexural modulus (stiffness) of PP by 7 and 5 % for PP-EBNS and PP-EBWS, respectively (Figure 5b). These results agreed with previously reported observations especially the incorporation of aragonite in relation to the neat PP matrix (Jing et al., 2018a). The overall differences between the PP-EBNS and PP-EBWS composites could be attributed to the incorporated particle's aspect ratios as well as their particle size distributions (Moczo & Pukanszky, 2019). This was interesting to observe as it demonstrated balanced material properties of the composites as desired by increasing the stiffness of the polymer matrix without negatively affecting its toughness (Zhang et al., 2012). The incorporation of commercial CaCO_3 into PP matrix to compare with aragonite recovered from the mine wastewater is a subject of ongoing investigations.

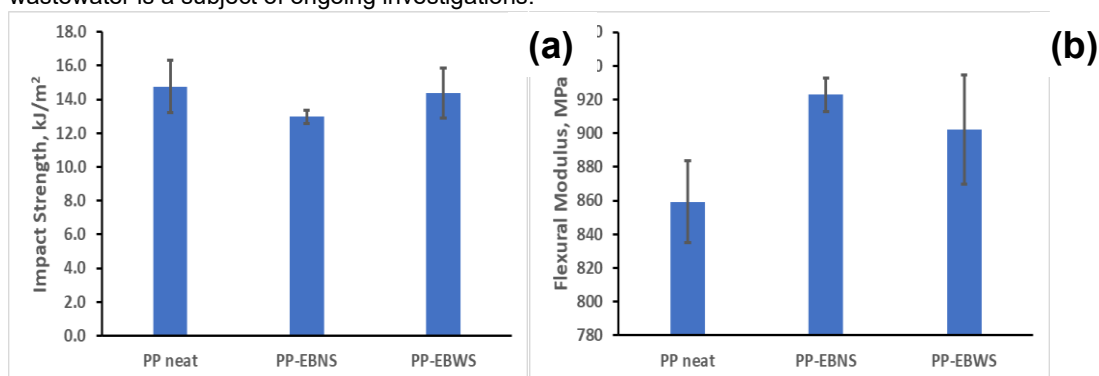


Figure 5: Mechanical properties of the composites (a) Impact strength, and (b) Flexural Modulus

4. Conclusions

This study was focussed on aragonite calcium carbonate recovered from the AMD of the Eastern basin in Gauteng, South Africa. The removal of suspended solids had an impact on the resulting particle's morphology and size distribution, and hence the different aspect ratios (8.7 vs. 7.2 for EBNS and EBWS, respectively). The particles did not have any influence on the polymer matrix crystalline phase. However, they did have a heterogenous nucleating effect, with PP-EBWS having the highest cooling crystallization peak at 122.1 °C vs. 120.8 °C for the virgin polymer. The particles also had a negative influence on the thermal stability of the matrix with the onset temperature of degradation reduced from 394 °C for the virgin polymer to 368 °C for the composites. The aragonite particles imparted good impact/toughness balance to the propylene copolymer (impact strength only decreased by 12 and 3 % for the PP-EBNS and PP-EBWS respectively) and flexural modulus increased by 7 and 5 % for the PP-EBNS and PP-EBWS respectively, thus demonstrating the industrial utility and environmental sustainability of the mineral recovered from acid mine drainage.

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