Eggshell, a new bio-filler for polypropylene composites

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Abstract

Chicken eggshell (ES) is an industrial byproduct containing 95% calcium carbonate, and its disposal constitutes a serious environmental hazard. Different proportions of chicken eggshell as bio-filler for polypropylene (PP) composite were compared with different particle sizes and proportions of commercial talc and calcium carbonate fillers by tensile test. The Young's modulus (E) was improved with the increment of ES content, and this bio-filler was better than all types of carbonate fillers with different particle sizes used in this study. Although ES composites showed lower E values than talc composites, talc filler could be replaced by up to 75% with ES while maintaining a similar stiffness and E compared to the talc composites. Scanning electron microscopy showed an improved interfacial bonding on the tensile fractured surface. The improvement in the mechanical properties was attributed to a better ES/matrix interface related to the geometric ratio of the ES particles similar to talc particles.

Keywords: Eggshell; Bio-filler; Polypropylene; Composite materials

1. Introduction

Composites are materials consisting of two or more identifiable constituents of different natures. Special consideration has been given to those composites which consist of synthetic fibers or mineral particles with a high modulus reinforcement embedded in a comparatively lower modulus matrix, such as polypropylene. However, due to the high cost of the petroleum-derived products or to environmental hazard, a growing effort has emerged in recent years on the research, development, and application of biocomposites. A biocomposite contains at least one constituent that is derived from renewable resources, such as avian feathers or cellulose fibers from kenaf, ramie, flax, sisal, coir, rice-husk and jute [1–4].

Polypropylene (PP) composites normally use inorganic fillers such as mineral calcium carbonate and talc [5–7]. Chicken eggshell (ES) is an aviculture byproduct that has been listed worldwide as one of the worst environmental problems, especially in those countries where the egg product industry is well developed. In the U.S. alone, about 150,000 tons of this material is disposed in landfills. 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 [8,9]. Although there have been several attempts to use eggshell components for different applications [10–16], its chemical composition and availability makes eggshell a potential source of filler for PP composites.

In a previous report we have shown, among other characteristics, that ES has a relatively lower density compared to mineral calcium carbonate (density values obtained by using ASTM 679 of 0.4236 g/cm^3 for eggshell as compared with 0.4670 of commercial calcium carbonate or 0.4581 of talk), and the ES–PP composite showed slightly higher crystallinity than similar PP composites made of mineral calcium carbonate (DSC measurements gave 48% of crystallinity as compared with 46% of commercial calcium carbonate or talk composites) [17,18]. These characteristics qualify ES as a good candidate for bulk quantity, inexpensive, lightweight and low load-bearing composite applications, such as the automotive industry, trucks, homes, offices, and factories.

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Table 1
Polypropylene composites: composite name, type, filler proportion, particle size and filler surface (BET) area

Composite name	Filler			
	Type	Proportion (% w/w)	Particle size (μm)	BET area (m^2/g)
PP–ES	ES [a]	40	8.4	18.0
PP–CC1	CC1 [b]	40	17.1	2.2
PP–CC2	CC2	40	2.0	3.2
PP–CC3	CC3	40	0.7	9.1
PP–TA1	TA1 [c]	40	10.7	4.6
PP–TA2	TA2	40	2.4	6.3
PP–TA3	TA3	40	0.5	11.9
PP–TA2–ES2	TA2/ES	20/20		
PP–TA3–ES2	TA3/ES	20/20		
PP–TA3–ES3	TA3/ES	10/30		

[a] ES = eggshell.
[b] CC = calcium carbonate.
[c] TA = talc.

In order to establish the effect of different fillers such as talc, commercial calcium carbonate and eggshell on the mechanical properties, the rigidity expressed as elastic or Young's modulus, is one of the most representative and appropriate properties normally used to characterize different fillers for selected applications with a single determination. In this article, we advance the data of Young's modulus (E) contained in the patent application [17,18] demonstrating the ability of ES as an alternative filler for PP composite compared with the traditional commercial reinforcements such as talc and mineral calcium carbonate.

2. Materials and methods

Mechanical test for E was carried out on different PP composite specimens (1.5 mm thick, 12 mm wide, and 120 mm long) composed of 40% w/w filler from different sources. Measurements were done under ASTM standard method D638 with a dynamometer model HP D500 at a cross-head speed of 50 mm/min at 23 °C and 32% relative humidity. SEM analysis was done on the fracture area of the tension tests with a TESLA BS 343A scanning electron microscope. Composites were made of PP homopolymer (melt flow index 12.5), antioxidant (Irganox 1010/Irgafos 168 (50/50)), and filled with the inorganic moiety as shown in Table 1. ES was obtained from White Leghorn hen eggs. Eggs were broken and the contents removed. The eggshells were dried at 90 °C for 8 h, mechanically triturated, and sieved to mesh 400. The PP, mineral fillers (talc or calcium carbonate), or ES, when appropriate, was mixed with 0.2% w/w antioxidant in a nitrogen atmosphere by using a Brabender Plasticorder model PLE331 internal mixer at 75 rpm at a temperature of 190 °C for 15 min. After blending, the composite was pelletized and then pressed to prepare the specimens for the mechanical test.

3. Results

All PP–filler composites showed a higher Young's modulus compared with the PP (Fig. 1). An increase in tensile modulus of the PP composites was observed when the particle size of the talc (TA) or calcium carbonate (CC) filler was decreased. PP–CC composites showed a smaller tensile modulus than PP–TA composites. Even with ES having a larger particle size than mineral calcium carbonate, the tensile modulus of the PP–ES composite is higher than that of the PP–CC composites. When the ES filler replaces up to 75% of the talc filler in the PP composite, the values of tensile modulus are at least as good as those obtained with the PP–talc composites. As seen in Fig. 2, the morphology of the ES filler is more like that of the talc than that of the mineral calcium carbonate. In fact, ES particles were better embedded in the PP matrix than were the calcium carbonate particles, and were equivalent to the talc particles in this regard (Fig. 3). Thus, ES particles show a phase continuity in the composite which is as good as or better than that displayed by particles of calcium carbonate or talc.

4. Summary and conclusions

In summary, the mechanical behavior of PP–ES composite shows a higher tensile modulus than the PP–CC composite with regard to particle size. A similar geometrical ratio of ES and talc particles could be the relevant factor in obtaining a hybrid composite of PP/ES/talc with similar modulus and homogeneity to that of the PP–TA composite. In conclusion, eggshells obtained from aviculture waste can easily be used as a filler for PP composites, which show better reinforcement properties

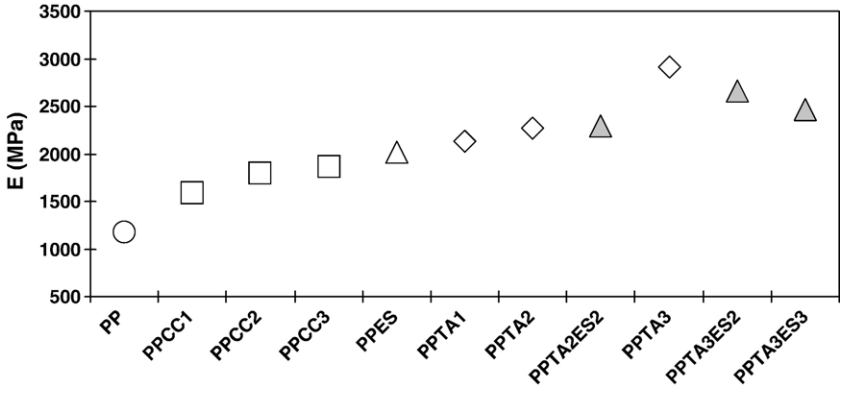

Fig. 1. PP–filler composites with 40% w/w filler: Young's modulus (E). Triangles represent composites containing eggshell.

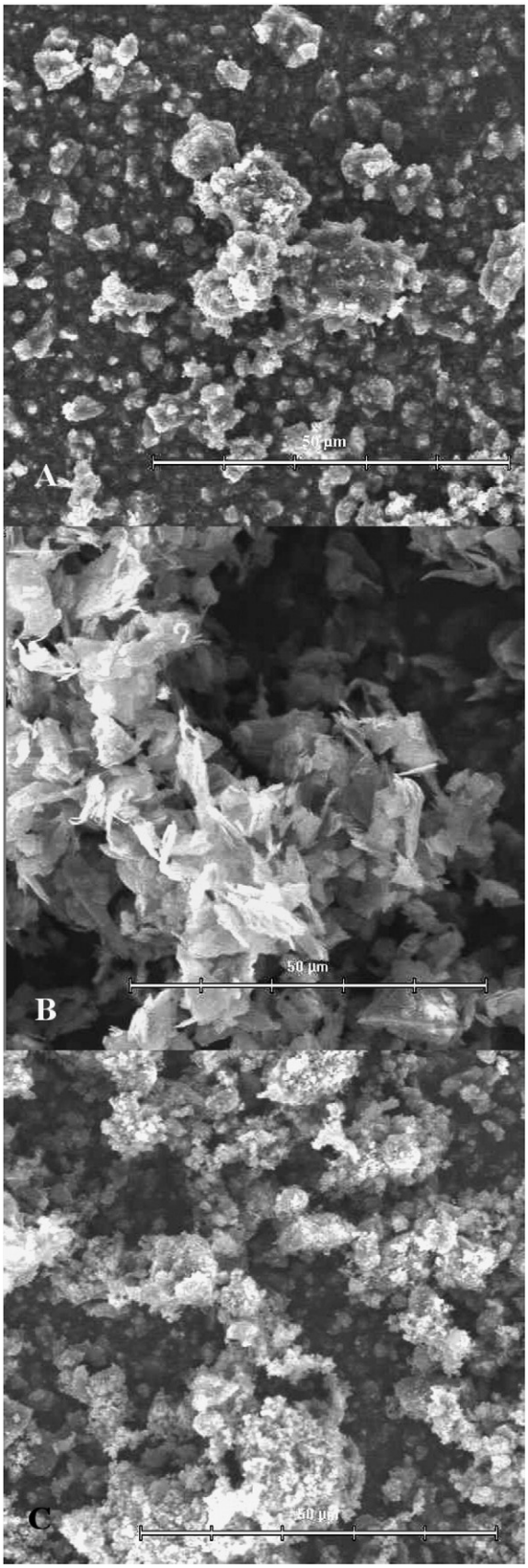

Fig. 2. SEM micrographs of the different fillers: A) calcium carbonate (CC2), B) talc (TA2), and C) eggshell (ES).

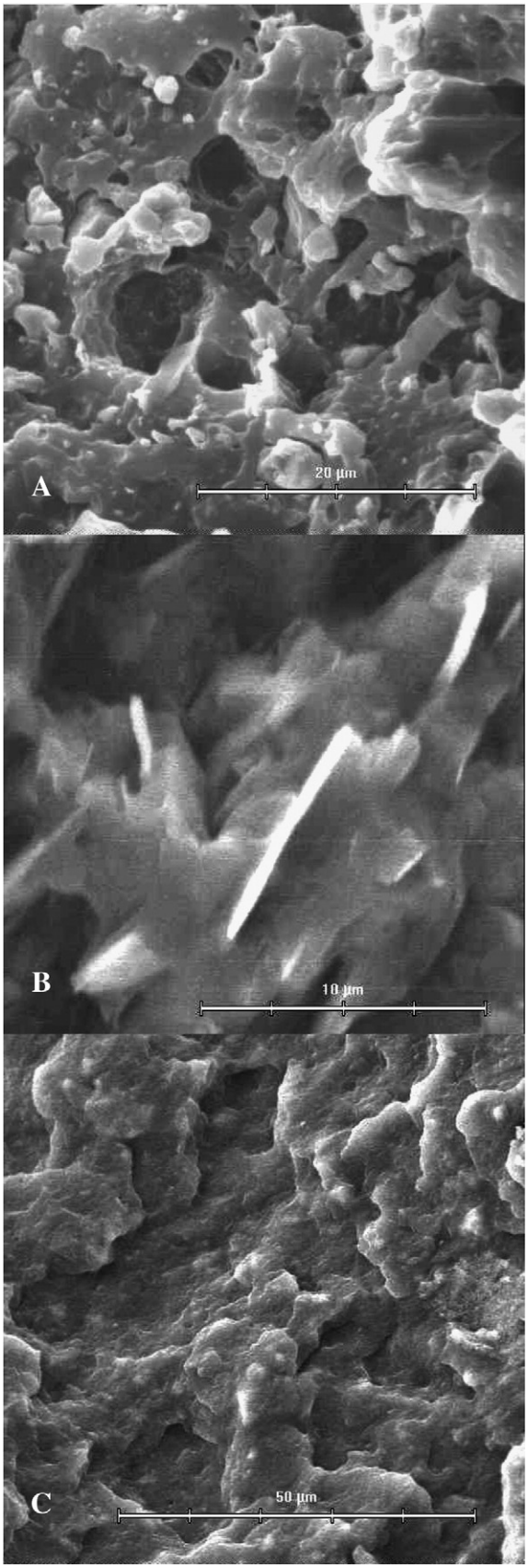

Fig. 3. SEM micrographs of the fracture surface of PP–filler composites with 40% w/w filler content: A) PP–CC2, B) PP–TA2, and C) PP–ES.

than composites made with traditional calcium carbonate filler, and can also replace talc to a great extent without decreasing the mechanical properties of the PP–TA composites.

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References

[1] T.A. Bullions, R.A. Gillespie, J. Price-O'Brien, A.C. Loos, J. Appl. Polym. Sci. 92 (2004) 3771.
[2] K.F. Fung, X.S. Xing, R.K.Y. Li, S.C. Tjong, Y.W. Mai, Compos. Sci. Technol. 63 (2003) 1255.
[3] C.A. Rodriguez, J.A. Medina, H. Reinecke, J. Appl. Polym. Sci. 90 (2003) 3466.
[4] P. Toro, R. Quijada, O. Murillo, M. Yazdani-Pedram, Polymer Int. 54 (2005) 730.
[5] B. Pukanszky, in: J. Karger-Kocsis (Ed.), Composites, vol. 3, Chapman & Hall, London, 1995.
[6] V. Svehlova, E. Poloucek, Angew. Makromol. Chem. 214 (2003) 91.
[7] W.C.J. Zuiderduin, C. Westzaan, J. Huétink, R.J. Gaymans, Polymer 44 (2003) 261.
[8] J.L. Arias, D.J. Fink, S.-Q. Xiao, A.H. Heuer, A.I. Caplan, Int. Rev. Cytol. 145 (1993) 217.
[9] J.L. Arias, M.S. Fernandez, Mater. Charact. 50 (2003) 189.
[10] S.I. Ishikawa, K. Suyama, K. Arihara, M. Itoh, Bioresour. Technol. 81 (2002) 201.
[11] S.I. Ishikawa, S. Sekine, N. Miura, K. Suyama, K. Arihara, M. Itoh, Biol. Trace Elem. Res. 102 (2004) 113.
[12] J.L. Liu, Q.S. Wu, Y.P. Ding, S.Y. Wang, J. Mater. Res. 19 (2004) 2803.
[13] J.L. Liu, Q.S. Wu, Y.P. Ding, Cryst. Growth Des. 5 (2005) 445.
[14] W.T. Tsai, J.M. Yang, C.W. Lai, Y.H. Cheng, C.C. Lin, C.W. Yeh, Bioresour. Technol. 97 (2006) 488.
[15] D. Xiao, M.M.F. Choi, Anal. Chem. 74 (2002) 863.
[16] F. Yi, Z.X. Guo, L.X. Zhang, J. Yu, Q. Li, Biomaterials 25 (2004) 4591.
[17] J.L. Arias, R. Quijada, M. Yazdani-Pedram, P. Toro, inventors. Chilean Patent Appl. N° 2542, (2004).
[18] J.L. Arias, R. Quijada, M. Yazdani-Pedram, P. Toro, inventors. Patent Appl. US-2006-068185-A1, (2006).