Preparation and Properties of Eggshell/β-Polypropylene Bio-Composites

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ABSTRACT: In this article, a novel eggshell/β-PP bio-composite was prepared and evaluated. First the waste chicken eggshell (ES) was modified by a stingy amount of pimelic acid (PA) through solution method, and then compounded with PP through melt blending method. The crystalline form, mechanical properties, and morphology of the ES/β-PP composites were studied. The results showed that ES modified by PA was a β nucleating agent with high efficiency and selectivity, resulting in the maximum K_β value of 0.99 in PP composites. PA modification promoted the dispersion and interfacial bonding of ES in PP. Although the addition of PA-modified ES slightly decreased tensile properties and flexural properties of PP, it increased the impact strength of PP by 228% than that of pure PP. Taking all factors into consideration, the optimal mass ratio of PP/ES/PA composites for reaching optimum mechanical properties should be 100/5/0.000471. Thus, the application of modified ES to prepare ES/β-PP bio-composites represents a promising way to mitigate environmental pollution and to reduce the cost of polyolefin products. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 125: 61–66, 2012

Key words: poly(propylene) (PP); mechanical properties; morphology; nucleation

INTRODUCTION

Polypropylene (PP) filled with mineral particles has gained importance as a result of many advantages, such as cost reduction, high modulus, improved dimensional stability, and reinforced thermal resistance.[1,2] In recent years, a growing effort has emerged on the research, development, and application of bio-fillers for preparation of bio-composites. Eggshell (ES) is an aviculture byproduct that has been listed worldwide as one of the worst environmental problems, and its disposal constitutes a serious environmental hazard. The ES constitutes by a three-layered structure, namely the cuticle on the outer surface, a spongy (calcareous) layer and an inner lamellar (or mammillary) layer[3] and contains about 95% $CaCO_3$ in the form of calcite and 5% organic materials such as type X-collagen, sulfated polysaccharides, and other proteins.[4] Therefore, ES must be a potential bio-filler for preparation of bio-composites with low cost and lightweight.

Recently, Toro et al.[5,6] compared the mechanical behavior of PP composite filled with chicken eggshell as bio-filler and those of PP composites filled with talc and calcium carbonate fillers. It is found that the increment of ES content improved the Young's modulus of PP and this bio-filler was better than all types of carbonate fillers. The mechanical behavior of ES/PP composite shows a higher tensile modulus than the $CaCO_3$/PP composite. Although ES composites showed lower Young's modulus than talc composites, talc filler could be replaced by up to 75% with ES while maintaining a similar stiffness and Young's modulus compared to the talc composites. 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. However, a decrease in impact strength and deformation at break with increase in filler content was observed. Therefore, it is suggested that eggshells obtained from aviculture waste can easily be used as a filler for PP composites, which show better reinforcement properties than composites made with traditional calcium carbonate filler, and can also replace talc to a great extent without decreasing the mechanical properties of the talc/PP composites.

Supri and coworkers[7,8] studied the effect of PE-*g*-MA on the tensile properties, morphology, and thermal properties of ES/LDPE composites. The tensile strength, elongation at break, and thermal stability

of ES/LDPE composites with PE-g-MA were higher than ES/LDPE composites, and their differences became more pronounced at higher filler content. The interfacial adhesion between ES and LDPE was improved with the addition of PE-g-MA. Kang et al.[9] investigated the effect of eggshell fibroin on morphology and thermal properties of SEBS as bio-filler.

In the ES/PP composites, addition of ES decreased the impact strength and deformation at break of PP as same as PP composites filled with excessive CaCO$_3$.[10–12] Although the crystal form of PP in ES/PP composites has no reported, α-crystal is generally formed in the PP composites filled with mineral fillers. It is well known that β-crystal of PP has higher impact strength than α-crystal of PP. If ES/β-PP composites were prepared, ES/PP composites with higher impact strength were obtained. Our research group has found that β-PP/CaCO$_3$ composites were prepared filled by using CaCO$_3$ modified by a small proportion of pimelic acid.[13–15] Therefore, we consider that ES/β-PP composites with higher impact strength are easy to prepare due to the ES containing about 95% CaCO$_3$. In this article, a novel ES/β-PP composite was prepared by using ES modified with pimelic acid and the crystallization behaviors, crystallization morphology, mechanical properties, and morphology of ES/β-PP composites are investigated.

EXPERIMENTAL

Materials

A commercial grade isotactic PP (HP500N, MFR = 12 g/10 min at 230°C) used in this study was supplied by Reliance Industries Limited. Dry chicken egg shell powder (denoted as ES) was obtained from a chicken farm in south China and was screened by a sieve with the hole of 100 meshes before being used. Chemical grade pimelic acid (PA) was purchased from Shanghai Hongsheng Industry Limited Company, China. Analytical grade acetone was provided by Guangzhou Chemical Reagent Factory, China.

Preparation of PA-modified ES

PA and ES were dried under vacuum at room temperature before being used. PA was mixed with ES in acetone solution with stirring at room temperature. Subsequently, acetone was vaporized for 6 h at room temperature to obtain PA-modified ES. The prepared PA-modified ES was denoted as ESx, where x means the times of mass ratio of ES/PA. Concretely, ES5, ES50, ES100, and ES200 indicated the ES/PA mass ratio of 5/1, 50/1, 100/1, and 200/1, respectively.

Preparation of ES/β-PP bio-composites

The ES/PP bio-composites and ES/β-PP bio-composites with ES/PP mass ratio of 1/100, 3/100, and 5/100 were homogenized at 190°C, and 50 rpm for 8 min using an HL-200 internal mixer (Jinlin University Science and Education Instrument Factory, China).

Mechanical testing

Tensile, flexural, and impact tests were carried out according to ASTM Standard. The test specimens were made on an injection molding machine at 190°C, with the mold temperature of 90°C and the cooling time of 30 s. For each type of composites, five specimens were tested and the average values were reported. Tensile tests were conducted according to ASTM D 638 using Type V specimen on a Universal Testing Machine (Zwick/Roell Z005, Zwick Roell Testing Machines) at a crosshead speed of 50 mm min^{-1}. Static flexual tests were carried out according to ASTM D 790 using the same Testing Machine mentioned above at a crosshead speed of 2 mm min^{-1}. Notched Charpy impact strength tests were conducted according to GB/T 1043 using a Universal Impact Testing Machine (ZBC-50, China Shenzhen SANS Testing Machine) and the notch was made through gear cutting method.

WAXD characterization

The Wide-angle X-ray diffraction testing specimens were cut from the mechanical testing specimens. The WAXD experiment was conducted with a Rigaku Geigerflex Model D/Max-III A rotating anode X-ray diffractometer. Graphite monochromatic Cu Kα radiation was employed as a radiation source. The scanning range was 5°–40° with the rate of 4° min^{-1} and a step length of 0.02. The content of the β-crystal of PP was determined according to standard procedures described in the literature,[16] employing the formula:

$$K_\beta = H_\beta(300)/(H_\beta(300) + H_\alpha(110) + H_\alpha(040) + H_\alpha(130)), \quad (1)$$

where $H_{\Omega(hkl)}$ denotes the intensity of respective (hkl) peak belonging to phase Ω.

SEM observation

The impact specimens were broken according to the impact property test conditions. The fracture surfaces of the specimens were sputter-coated with gold before conducting a scanning electron microscope (SEM) analysis. The fracture surface morphology of the composites was observed on a Philips XL-30 ESEM microscope with an acceleration voltage of 15 kV.
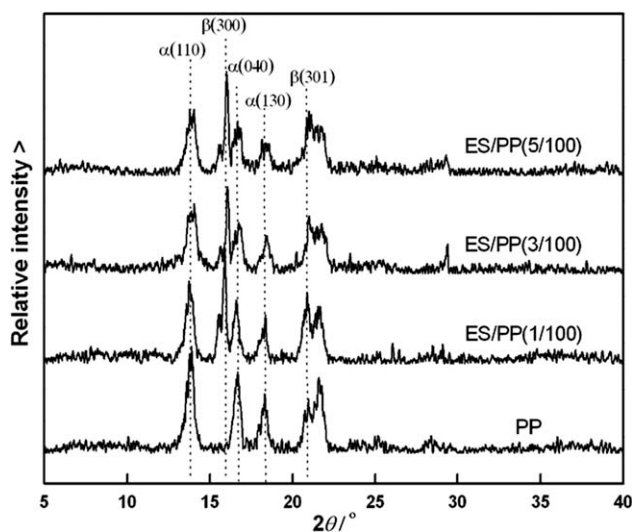
Figure 1 WAXD patterns of PP and ES/PP composites.

DSC analysis

The crystallization behavior and melting characteristics of ES/PP bio-composites and ES/β-PP bio-composites were carried on a TA DSC Q10 differential scanning calorimeter (DSC). The temperature and the enthalpy have been calibrated with indium at different rates in our experiments. About 5 mg of the sample was weighed very accurately. The sample was heated up to melting temperature of 220°C and held for 5 min to erase the thermal and mechanical history. After premelting, the sample was cooled to 50°C at the rate of 10°C min^{-1} for crystallization behavior investigation, and then reheated to 220°C at the rate of 10°C min^{-1} for melting behavior and polymorphism investigation. All DSC curves in this article have been normalized.

RESULTS AND DISCUSSION

Crystalline form of ES/PP composites and ESx/PP composites

Figure 1 presents X-ray diffraction diagrams of PP and ES/PP composites with different content of ES. Table I shows the K_β values of the samples calculated by eq. (1). The K_β value of pure PP was close to zero. Although addition of ES and the increase in ES content increased the K_β value of PP, the K_β value of ES/PP composites is below 0.2. Thus, ES is a kind of weak β nucleating agent as same as CaCO$_3$. Figure 2 shows X-ray diffraction diagrams of ES100/PP composites. The K_β values are listed in Table I.

It can be observed that the K_β value of ES100/PP composites was much higher than that of ES/PP composites and reached above 0.9. It is indicated that ES100/β-PP composites were obtained. Figure 3 shows X-ray diffraction diagrams of ESx/PP (5/100) composites with different PA content. It can be seen

TABLE I
K_β Values of PP, ES/PP Composites, and ESx/PP Composites

Sample	PA content in composite ($\times 10^{-4}$ wt %)	K_β
PP	0	0.01
ES/PP(1/100)	0	0.14
ES/PP(3/100)	0	0.20
ES/PP(5/100)	0	0.16
ES100/PP(1/100)	0.98	0.93
ES100/PP(3/100)	2.88	0.98
ES100/PP(5/100)	4.71	0.98
ES200/PP(5/100)	2.37	0.97
ES50/PP(5/100)	9.34	0.99
ES5/PP(5/100)	79.36	0.60

that the K_β values were above 0.9 for ESx/PP (5/100) composites with different PA content except the ES5/PP composite. Our previous study showed that pure PA played α nucleation effect on PP crystallization.[14] In the ES5/PP composite, there was up to 79.36 × 10^{-4}wt % of PA which exceeded the amount of the CaCO$_3$ on the ES surface. The excessive PA entered into PP and induced the formation of α-PP.

Above results indicated that ES100/β-PP composites are easily to preparation by ES modified by PA. Compared with other β-nucleating agents, for example calcium pimelate, the content of PA is significantly decreased. In the ES100/PP(5/100) composite filled by ES/PA = 100/1, the formed calcium pimelate content was about 4.71 × 10^{-4}wt % in the composite, the K_β value reached 0.98. It is indicated that the ESx bio-filler with β-nucleation prepared in our lab not only possesses high β-nucleating ability, but also low cost for preparation of β-PP composites. It is noteworthy that the ES200/PP(5/100) composite with less PA content and more ES content still remained excellent β nucleating ability. This is of
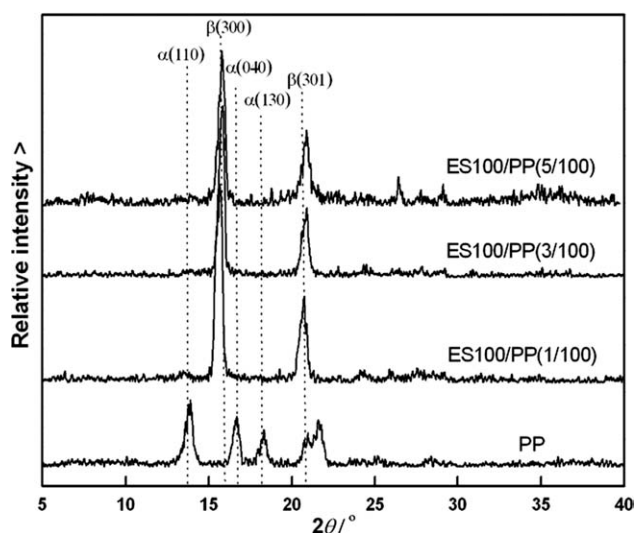
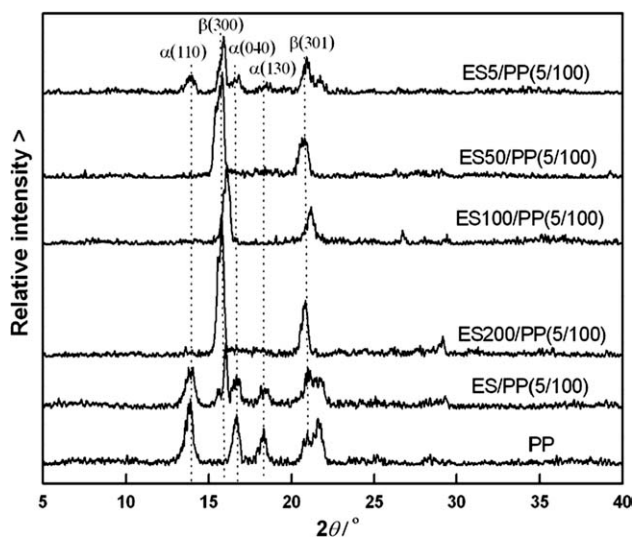

Figure 2 WAXD patterns of ES100/PP composites.

Figure 3 WAXD patterns of ESx/PP(5/100) composites.

great significance to the decrease the cost of β-PP composites and the high value use of waste ES.

Mechanical properties of ESx/PP composites

Tensile, flexural, and impact properties of PP, ES/ PP, and ESx/PP composites were listed in Table II. It can be observed that the addition of ES and the increasing content of ES slightly decreased the tensile strength (TS) of PP, and increased the flexural strength (FS) and flexural modulus (FM) while improved the notched Charpy impact strength (IS). In the composite with ES/PP mass ratio of 3/100, the IS increased from 2.1 kJ m^{-2} of pure PP to 3.1 kJ m^{-2}. It is suggested that the decreased TS of PP is attributed to the poor compatibility of hydrophilic unmodified ES and hydrophobic PP. The strengthening of ES resulted in increased FS and FM of PP composite and the formation of a certain amount of β-PP in composites improved the IS of PP composite.

In the ESx/PP composites, the TS and FS were lower than that of ES/PP composites and pure PP. However, the IS of ESx/PP composites was higher

than that of ES/PP composites. In the ES100/PP(5/ 100) composite, the IS increased by 214 and 112% compared to pure PP and ES/PP composite, respectively. The decreased TS and improved IS are mainly attributed to the effect of β-PP with low tensile strength and high IS. In the ESx/PP composites, the K_β values were up to 0.9 and high β-PP content led to the substantial improvement of IS in ES/PP composites.

## SEM observation of ESx/PP composites

Figure 4 shows the SEM pictures of the fracture surfaces of PP, ES/PP, and ES100/PP composites. The fracture surface of pure PP was smooth and flat, belonged to the typical brittle fracture. The fracture surface of ES/PP composite was coarse; meanwhile, drawing thread phenomenon that can absorb a large amount of impact energy appeared. Also, there had been some ES particles with the sizes between 2 and 50 μm on the fracture surface, and the interface between the ES particle and PP matrix was obvious. On one hand, ES induced PP to form a certain amount of β-PP. Thus, the absorbing amount of impact energy was improved. On the other hand, the poor compatibility of ES and PP made crack propagate along the interface between the ES particle and PP matrix, which decreased the absorbing amount of impact energy. The fracture surface of ES100/PP composite was accidented, and white ES particle adhered with the matrix tightly, indicating the crack propagating along the PP matrix. Because the much higher content of β-PP was contained in PP matrix, crack propagation encountered a large amount of hindrance, which led to the accidented fracture surface. This also suggested that the organic pimelic acid modification promoted the dispersion and interfacial bonding of ES in PP matrix.

## Crystallization and melting behavior of ESx/PP composites

During the blending process, the CaCO$_3$ on the ES surface modified by PA would react with PA to

TABLE II
**Mechanical Properties of PP, ES/PP Composites, and ESx/PP Composites**

Sample	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Notched charp impact strength (kJ m^{-2})
PP	33.4 ± 0.4	15.6	24.7 ± 0.4	1004 ± 53	2.1 ± 0.3
ES/PP(1/100)	33.4 ± 0.2	7.1	26.0 ± 0.3	1070 ± 43	2.9 ± 0.2
ES/PP(3/100)	32.7 ± 0.6	6.7	26.0 ± 0.2	1110 ± 50	3.1 ± 0.6
ES/PP(5/100)	32.3 ± 0.3	6.6	26.2 ± 0.2	1123 ± 15	3.1 ± 0.3
ES100/PP(1/100)	30.8 ± 0.4	7.6	21.2 ± 0.3	964 ± 32	4.8 ± 0.5
ES100/PP(3/100)	30.1 ± 0.2	6.7	21.6 ± 0.1	1010 ± 16	6.0 ± 0.5
ES100/PP(5/100)	29.3 ± 0.4	6.4	22.3 ± 0.1	1060 ± 10	6.6 ± 0.5
ES200/PP(5/100)	29.3 ± 0.3	6.2	22.6 ± 0.2	1073 ± 37	6.6 ± 0.2
ES50/PP(5/100)	29.6 ± 0.3	6.5	22.2 ± 0.2	1030 ± 10	6.9 ± 0.6
ES5/PP(5/100)	32.7 ± 0.6	5.8	29.6 ± 0.4	1396 ± 11	4.8 ± 0.4
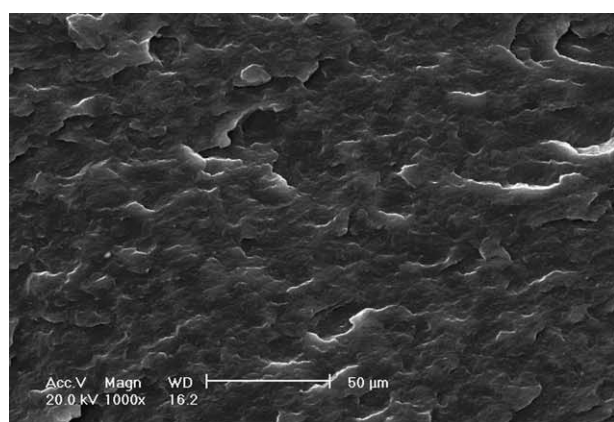
(a) PP
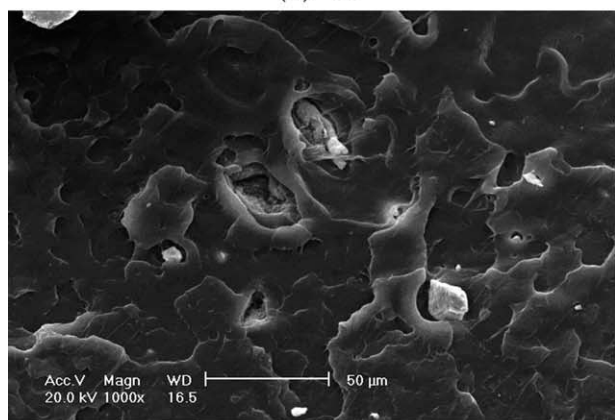
(b) ES/PP (3/100)
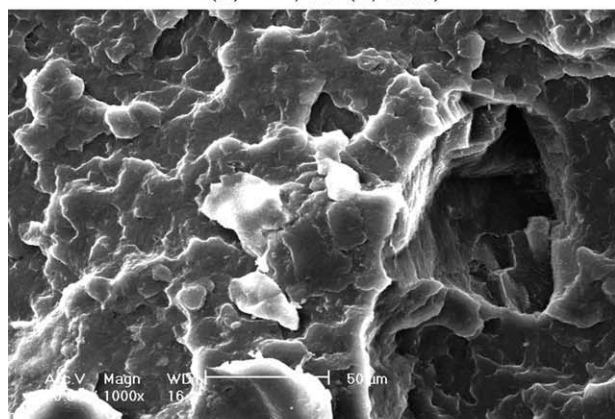
(c) ES100/PP (3/100)

Figure 4 SEM pictures of the fracture surfaces of PP, ES/PP composites, and ES100/PP composites.

form calcium pimelate which is a β-nucleating agent for PP crystallization. The ES with α-nucleation was changed into β-nucleation and the bio-filler with β-nucleating activity was obtained. Figure 5 shows the DSC crystallization and melting curves of ES100/PP composites. Related data can be seen in Table III. Compared with that of unmodified ES, the addition of ES100 significantly increased the T_c of PP. When the ES100/PP mass ratio was 1/100, the T_c of composite increased from 115.5°C of pure PP to 120.0°C.

Further increase the ES100 content and the T_c of composite will gradually increased. Obviously, ES modified by PA exhibited heterogeneous nucleation for PP crystallization. It can be seen from Figure 5(b) that only one melting peak of PP was observed at temperature of 163°C, which is attributed to melting of α-crystal of PP. However, the melting curves of ES100/PP(1/100) composites show two melting peaks at temperature of 150 and 154°C, which is in accordance with the melting of $β_1$-PP and $β_2$-PP in the composites. No melting peak was observed for α-crystal of PP. The intensity of melting peak for $β_2$-PP decreased and disappeared with increasing the ES100 content.

CONCLUSIONS

In this study, a new-type eggshell/β-PP bio-composite was successfully prepared by melt
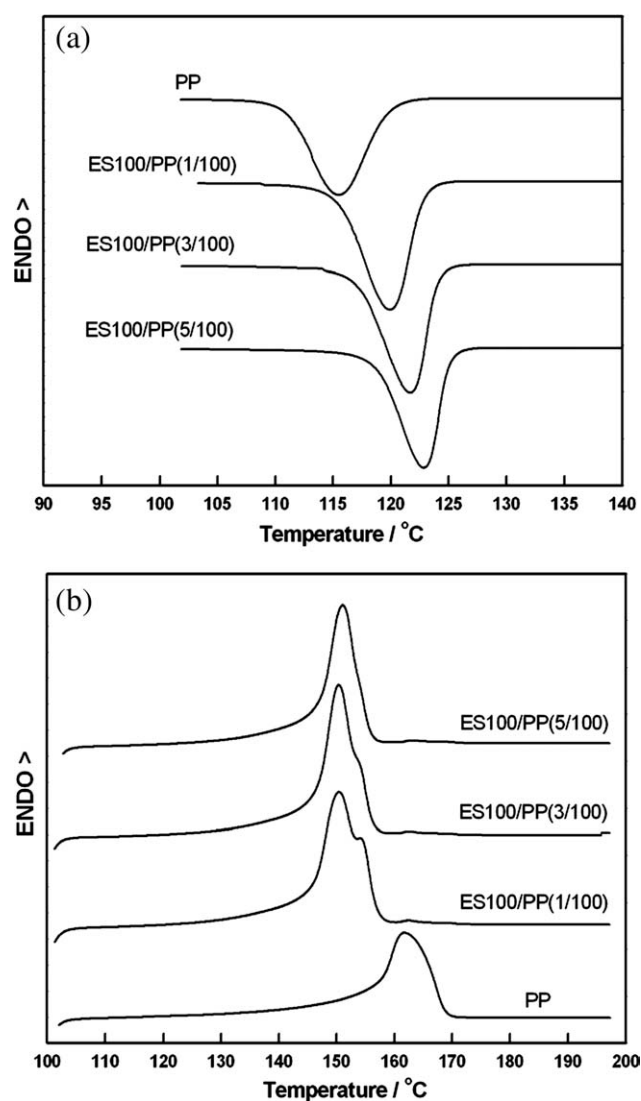

Figure 5 Crystallization (a) and melting (b) curves of ES100/PP composites.

TABLE III
DSC Data of PP, ES/PP Composites, and ES100/PP Composites

Sample	T_c (°C)	ΔH_c (g J^{-1})	T_m (°C)$\beta/\alpha_1/\alpha_2$	ΔH_m (g J^{-1})$\beta/\alpha_1/\alpha_2$
PP	115.5	100.0	161.8/−/−	96.8/−/−
ES/PP(1/100)	115.3	97.1	146.7/153.7/161.6	7.6/2.1/95.4
ES/PP(3/100)	115.1	95.7	146.5/153.6/162.2	5.9/1.9/93.5
ES/PP(5/100)	114.9	94.2	146.4/153.6/162.8	3.0/1.0/89.8
ES100/PP(1/100)	120.0	88.4	150.4/−/162.9	93.6/−/0.9
ES100/PP(3/100)	121.7	89.0	150.4/−/163.0	95.5/−/0.9
ES100/PP(5/100)	122.9	86.2	151.0/−/163.5	93.7/−/1.2

compounding PP and chicken eggshell (ES) modified with pimelic acid. The modified ES exhibits high efficiency and selectivity to the formation of β-PP and results in the maximum β-PP content of 99% in PP composites. The β nucleating ability of PA-modified ES was mainly determined by the content of both ES and PA. PA modification promoted the dispersion and interfacial bonding of ES in PP. Although the addition of PA-modified ES slightly decreased the tensile properties and flexural properties of PP, it increased the impact strength of PP by 228% than that of pure PP. Based on the comprehensive consideration, the optimal mass ratio of PP/ES/PA of the composites for reaching optimum mechanical properties was 100/5/0.000471. Furthermore, adjusting the content of ES and PA can modulate the ratio of β-PP and α-PP in PP composites. As a result, PP composites with strengthening and toughening capabilities are expected to be obtained. The optimum ratio of β-PP and α-PP is about 6 : 4. To sum up, the application of modified ES to prepare ES/β-PP bio-composites with high performance is not only feasible but also represents a promising way to mitigate environmental pollution and to reduce the cost of polyolefin products.

References

1. Albano, C.; Gonzalez, J.; Ichazo, M.; Rosales, C.; Urbina de Navarro, C.; Parra, C. Compos Struct 2000, 48, 49.
2. Hartikainen, J.; Hine, P.; Szabo, J. S.; Lindner, M.; Harmia, T.; Duckett, R. A.; Friedrich, K. Compos Sci Technol 2005, 65, 257.
3. Tullett, S. G. In Egg Quality—Current Problems and Recent Advances; Wells, R. G., Belyavin, C. G., Eds.; Butterworths: London, 1987, p 123.
4. Arias, J. L.; Fink, D. J.; Xiao, S. Q.; Heuer, A. H.; Caplan, A. I. Int Rev Cytol 1993, 145, 217.
5. Toro, P.; Quijada, R.; Yazdani-Pedram, M.; Luis Arias, J. Mater Lett 2007, 61, 4347.
6. Toro, P.; Quijada, R.; Arias, J. L.; Yazdani-Pedram, M. Macromol Mater Eng 2007, 292, 1027.
7. Shuhadah, S.; Supri, A. G. J Phys Sci 2009, 20, 87.
8. Supri, A. G.; Ismail, H.; Shuhadah, S. Polym Plast Technol Eng 2010, 49, 347.
9. Kang, D.; Pal, K.; Park, S.; Bang, D.; Kim, J. Mater Des 2010, 31, 2216.
10. Zhang, Q.; Yu, Z.; Xie, X.; Mai, Y. Polymer 2004, 45, 5985.
11. Chan, C.; Wu, J.; Li, J.; Cheung, Y. Polymer 2002, 43, 2981.
12. Zebarjad, S. M.; Sajjadi, S. A.; Tahani, M. J Mater Process Technol 2006, 175, 446.
13. Zhang, Z.; Wang, C.; Yang, Z.; Chen, C.; Mai, K. Polymer 2008, 49, 5137.
14. Zhang, Z.; Tao, Y.; Yang, Z.; Mai, K. Eur Polym Mater 2008, 44, 1955.
15. Zhang, Z.; Chen, C.; Wang, C.; Zhang, J.; Mai, K. Polym Int 2010, 59, 1199.
16. Turner-Jones, A.; Aizlewood, J.; Beckett, D. Macromol Chem Phys 1964, 75, 134.