Mechanical Strengths of Epoxy Resin Composites Reinforced by Calcined Pearl Shell Powders

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ABSTRACT: A series of epoxy resin (EP) composites were prepared using ground pearl shell powders, which had been calcined at various temperatures. The EP composite containing $\sim$ 3% weight content of the calcined pearl shell powder had the highest impact strength and the presence of silane agent was found to be essential for the composite formulation. The impact strengths of the resultant EP composites were highly influenced by the specific surface area, surface morphological structure, and chemical composition of the calcined pearl shell powder. The highest mechanical improvement was obtained for the EP composite prepared with the pearl shell powder calcined at 700°C for 3 h. The layered biopolymeric materials were completely degraded for the pearl shell powder calcined at 700°C, resulting in "sponge-like" or "net-like" porous calcium carbonate powder. However, the degradation of the layered biopolymeric materials was not complete for the calcinations at lower temperatures (<600°C), while calcium carbonate decomposed to form calcium oxide at higher temperatures (>800°C). The mechanical improvements of the processed EP composites have been discussed along with the chemical compositions and surface microstructures of the incorporated pearl shell powders. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3168–3176, 2009

Key words: epoxy resin composite; calcium carbonate; calcium oxide; pearl shell powder; calcination; impact strength

INTRODUCTION

Epoxy resins (EP) are important thermosetting commodity polymers and have many outstanding physical, chemical, and mechanical features making them attractive for a wide range of automotive and aerospace applications, and also for structural, adhesive, and electronic devices.[1] However, EP are fairly brittle (low toughness) and susceptible to impact-induced damage (poor crack resistance), which may lead to severe safety problems and thereby limit their many potential applications. The most successful method of improving the toughness of EP has been incorporated a second phase of dispersed organic/inorganic particulate fillers.[2] A variety of inorganic particulate fillers, such as calcium carbonate, silica, glass beads, silicon carbide, etc., have been used to improve the mechanical performance of EP.[3] Calcium carbonate is one of the most common inorganic particulate fillers used to improve the strength and toughness of polymer products as it is relatively easily dispersed in EP matrixes.[4] Moreover, calcium carbonate has been widely used as an additive or modifier in paper, paints, plastics, inks, coatings, adhesives, agriculture, etc.

Calcium carbonate is the primary component ($\sim$ 95%) of pearl shells (nacre).[5] Pearl shells are the main waste of the pearl industry, which discards millions of tons of pearl shells annually to landfills in China. Pearl shells are a biogenic hybrid composite consisting of alternating layers of calcium carbonate tablets with a width between 5 and 20 μm and a thickness between 0.5 and 1.0 μm, separated by 30–50 nm layers of elastic biopolymers.[5–7] These thinly layered biopolymers are primarily composed of hydrophobic proteins and chitins, which act as an adhesive connecting the calcium carbonate layers to maintain structural integrity.[6] The pearl shell's outstanding mechanical performance has been attributed to the "brick and mortar" hybrid structure.[7] For example, the mechanical strength of pearl shells is up to 3000 times greater than that of pure calcium carbonate.[7] Although the majority of the pearl shell is calcium carbonate, pearl shells are extremely stable under normal weather conditions.[8,9] However, the hydrophobic protein and/or chitin molecules, the main components of the biopolymer layers of pearl shells, completely decompose into gaseous

products at around 300°C,[10,11] suggesting that calcium carbonate could be obtained from calcination of the pearl shell powder since the less stable aragonite will only decompose into calcium oxide at around 825°C.[12]

The aim of the present article is to investigate the mechanical properties of the EP composites prepared using the abundant pearl shell powders after being calcined at different temperatures. Effects of the calcination temperatures were first examined through analysis of the physical properties and surface morphological structures of the pearl shell powders since the size, surface microstructure and chemical composition of the inorganic fillers have significant effects on the mechanical properties of the composites.[13] The mechanical improvements of the resultant EP composites were examined and discussed along with the chemical composition, physical properties, and surface microstructures of the calcined pearl shell powder.

EXPERIMENTAL SECTION

Materials

Diglycidyl ether of bisphenol A (DGEBA) was used as the EP monomer (epoxide value 0.511 eq/100 g), and 4,4′-methylenedianiline was used as the curing agent (amine hardener). Both DGEBA and 4,4′-methylenedianiline were purchased from Jiangyin Wayfar Synthetic Material Company (Jiangsu, China). Silane coupling agent (3-aminopropyltriethoxysilane) was purchased from Feidian Chemical Company (Hangzhou, Zhejiang, China). Analytical grade acetone was purchased from Dafang Chemical Reagent Company (Hangzhou, Zhejiang, China). Pearl shells were obtained from Zhuji Pearl Shell Farm (Zhuji, Zhejiang, China).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements of the ground pearl shell powder

The pearl shells were first cleaned to remove debris and then ground into powder ($\sim$ 5 μm). The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms were recorded on a STA 409PC (NETZSCH-Gerätebau GmbH, Germany) at a heating rate of 10°C /min up to about 1000°C in the presence of oxygen. The pearl shell powder samples were balanced for about 30 min before each analysis.

General procedure for calcination of the ground pearl shell powder

The pearl shell powder samples were calcined in a furnace at 150, 200, 300, 600, 700, 800, and 900°C, respectively, for 3 h and then transferred into a desiccator at ambient temperature until analysis or application.

General procedure for characterization of the calcined pearl shell powder

The calcined pearl shell powder samples were first degassed at 300 K for 6.0 h at high vacuum ($<10^{-3}$ torr) before analysis measurements. The specific surface area (BET) and pore volume of the calcined pearl shell powder were measured by nitrogen (N_2) gas adsorption at 77 K using an ASAP2020 M (Micromeritics) apparatus (Norcross, GA). Oil absorbent values were determined according to the national standard GB/T3780.2-2003. Infrared (IR) spectra were recorded in the range of 500–4000 cm^{-1} on a Nicolet Nexus Fourier Transformed Infrared spectrometer (Nicolet Instrument Company, Madison, WI). Contact angle (H_2O) measurements were conducted according to ASTM D5725-99, using a 500 senior contact angle instrument (Disuo Chemical Analytical Instrument Company, Beijing, China). X-ray diffraction (XRD) measurements were performed on an Xppert 2 MRD (Philips Company, Washington DC) with CuKα as a radiation source, operating at 40 kV and 30 mA. The surface morphology of the pearl shell powder and the EP composites was examined using a scanning electron microscopy (SEM) (JSM-5600LV, Nippon Electronics Company, Japan) with an acceleration voltage of 20 kV or 25 kV. The EP composite samples were coated with a gold layer before the analysis to improve the SEM measurement sensitivity.

General procedure for preparation of the EP composites using the calcined pearl shell powder

The calcined pearl shell powder (3.0 g) was suspended in 50 mL of acetone in a flask with or without the addition of 3-aminopropyl triethoxysilane (0.3 g). The mixture was stirred at ambient temperature for 1 h, followed by the removal of the solvent acetone. The residue was then mixed with bisphenol A-type EP monomer (DGEBA) and the hardener (97 g) and vigorously stirred at 90°C for 30 min. After a stoichiometric amount of hardener 4,4′-methylenedianiline was added, the mixture was vigorously agitated for another 10 min, and then poured into a release-coated steel mold. The curing procedure for the EP composites was set for 2 h at 90°C and then 5.0 h at 150°C to form 6.0 mm EP composite plates for the related impact strength measurements. Five specimen samples were prepared for each EP composite.

Impact strength measurements of the EP composites

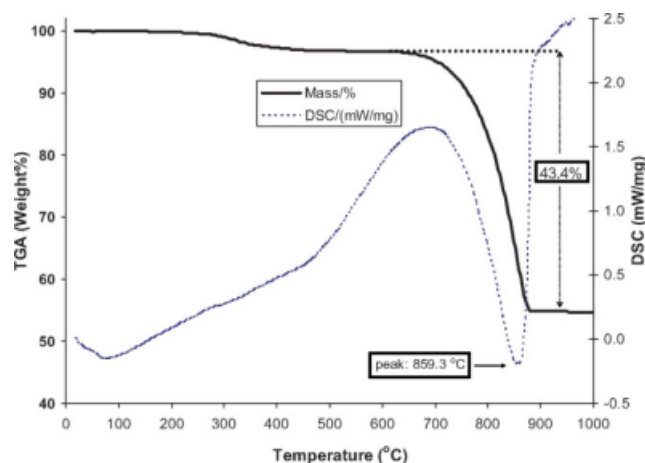The single-edge-notched impact strength measurements were performed with the 6.0 mm EP composite

Figure 1 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermograms of the ground pearl shell powder. Heating rate: 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

plates according to the national standard GB/T/2571-1995V, using a XJJ-5 simple beam impact testing instrument (Chengde Testing Machine Plant, Sichuan, China). The reported impact strength for each EP composite is an average of five independent measurements.

RESULTS AND DISCUSSION

Thermal analysis of the ground pearl shell powder

The thermograms of the TGA and DSC measurements were summarized in Figure 1 for the ground pearl shell powder. Examination of the TGA curve in Figure 1 shows that the weight loss (w/w) is less than 5% until 700°C, presumably due to the degradation of the layered biopolymeric materials. The 43.4% weight loss around 900°C can be attributed to the weight loss of carbon dioxide gas from calcium carbonate decomposition, i.e. $MW_{CO_2}/MW_{CaCO_3} = 44.01/100.1 = 44\%$. These results are consistent with the literature that the primary component ($\sim$ 95%) of pearl shells is calcium carbonate.[5] The DSC thermogram of Figure 1 shows a large

endothermic transition, which mirrors the weight loss of carbon dioxide gas from the TGA thermogram. The peak temperature for the endothermic transition is 859°C, which is close to the decomposition temperature (825°C) of aragonite calcium carbonate.[12]

Physical properties of the calcined pearl shell powders

To assess the thermal degradation of the layered biopolymeric materials, the ground pearl shell powder was calcined at 150, 200, 300, 600, 700, 800, and 900°C, respectively, for 3 h. The calcined shell powders were characterized by determination of the specific surface area (BET), pore volume, oil absorbent value together with contact angle, and the related results were summarized in Table I.

Examination of Table I shows that the specific surface area (BET), pore volume and oil absorbent value of the calcined pearl shell powder increase with the calcination temperature. The much larger specific surface area, pore volume and oil absorbent value of the pearl shell powder calcined at 600 or 700°C than those calcined at 150, 200, or 300°C are clearly associated with the much quicker decomposition of the layered biopolymeric materials at higher calcination temperatures. Nevertheless, the pore sizes resulting from the degradation were expected to be in the dimension of the biopolymer layers, i.e. 30–50 nm. The dramatic decrease of the contact angle (water) (Table I) must be associated with decomposition of the hydrophobic proteins and chitins of the particle surface biomacromolecules. In other words, the higher calcination temperatures accelerated degradation of the hydrophobic biomacromolecules, resulting in the porous particle surface of hydrophilic calcium carbonate.

Surface structures of the calcined pearl shell powder

The surface structure of the particulate filler is critical for its interfacial interaction with the polymer matrix molecules.[4] The scanning electron microscopic

TABLE I
Dependence of the Physical Properties of the Pearl Shell Powders with the Calcination Temperatures

Temperature (°C)	150	200	300	600	700	800	900
BET[a]	4.0	4.1	4.4	7.9	18.5	19.2	21.3
Pore volume[b]	0.020	0.020	0.022	0.028	0.052	0.067	0.047
Oil absorbent value[c]	35	35	40	48	72	80	75
Contact angle (H$_2$O)	85.3	85.6	75.2	24.8	18.2	24.3	29.6

[a] Specific surface area (BET) (m^2 g^{-1}).
[b] Pore volume (cm^3 g^{-1}).
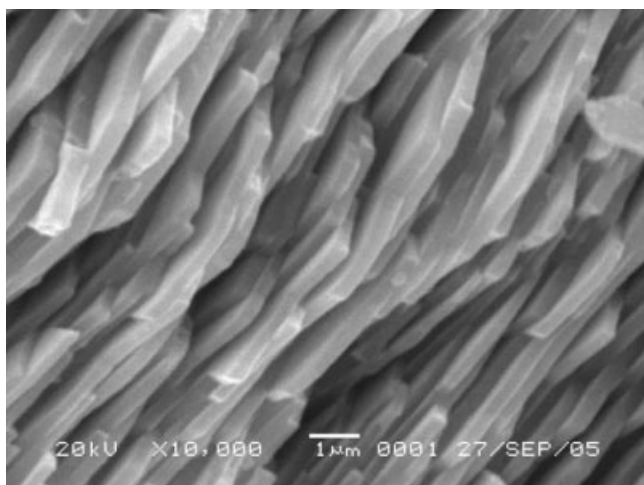[c] Oil absorbent value (g/100 g).

Figure 2 Scanning electron microscopy (SEM) image of the cross section of the fractured pearl shell (nacre).

(SEM) image of a pearl shell indicates that the fractured cross section surface is flat and smooth as shown in Figure 2. But after being calcined at 200°C for 3 h, the surface of the pearl shell powder becomes blurred as shown in Figure 3, presumably due to partial degradation of the surface biopolymer molecules. Most intriguingly, the pearl shell powder becomes fluffy like cotton after being calcined at 700°C for 3 h as shown in Figure 4. Formation of the sponge-like or net-like calcium carbonate powder could be attributed to the complete degradation of the layered biopolymeric materials. These results are consistent with the significant increase of the specific surface area and the pore volume (Table I) of the pearl shell powders after being calcined at 600 and 700°C. It is interesting to note that the sponge-like nanostructured porous calcium carbonate derived from calcination is structurally different with the spherical calcium carbonate
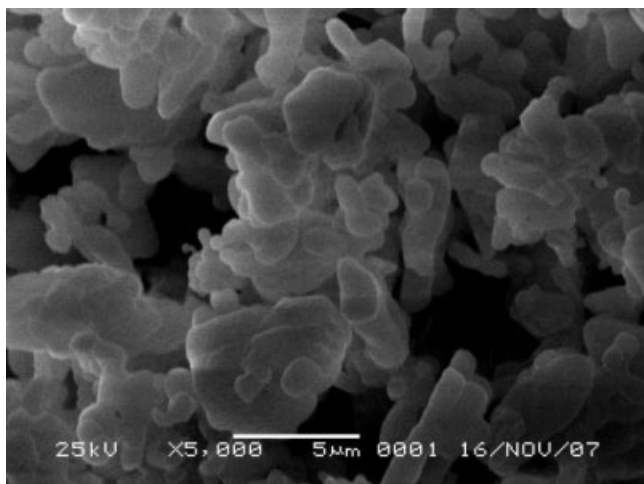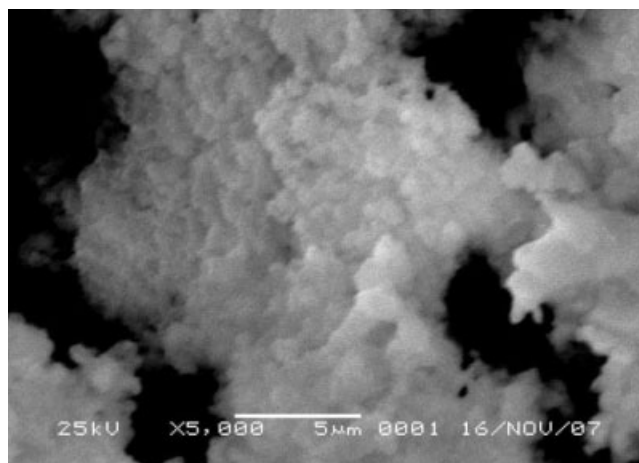

Figure 4 Scanning electron microscopy (SEM) image of the pearl shell powder after being calcined at 700°C for 3 h.

nanoparticles obtained from other methods such as the wet chemical reactions.[14]

Polymorphs and decomposition of calcium carbonate

Of calcium carbonate's three different polymorphs, i.e. calcite, aragonite and vaterite, calcite is the most thermodynamically stable form. Each calcium carbonate polymorph has a specific XRD pattern, which can be used to characterize the crystallographic structures.[15]

The XRD spectra of the calcined pearl shell powders were summarized in Figure 5. The characteristic XRD peaks labeled as "a" specify for aragonite and those labeled as "c" specify for calcite. Although aragonite is thermodynamically less stable than calcite, the calcium carbonate of pearl shells is
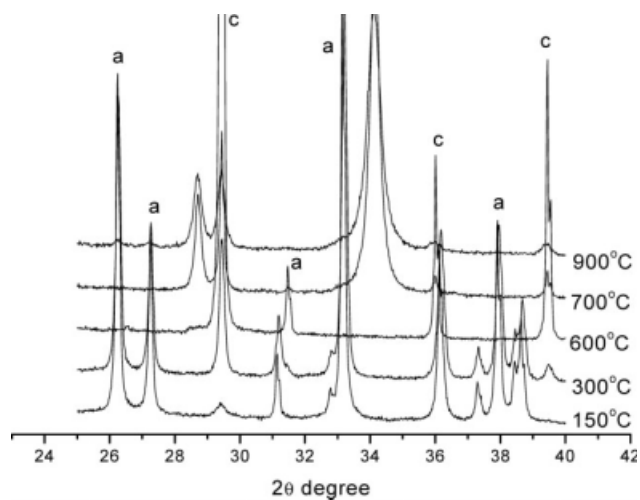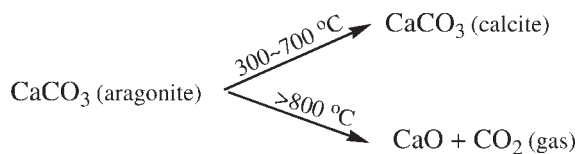

Figure 3 Scanning electron microscopy (SEM) image of the pearl shell powder after being calcined at 200°C for 3 h.

Figure 5 X-ray diffraction (XRD) spectra for the calcined pearl shell powders. XRD peaks labeled as "a" for the aragonite calcium carbonate and labeled as "c" for the calcite calcium carbonate.

Scheme 1 Morphological transformation and decomposition of calcium carbonate.

exclusively in the aragonite form.[6,7] Examination of Figure 5 shows that the calcium carbonate of the pearl shell powder was still in the aragonite form after being calcined at 150°C for 3 h, indicating that there was no morphological transformation for the calcium carbonate at 150°C for 3 h. However, the XRD spectrum indicates that some of the calcium carbonate in the pearl shell powder was transformed into the thermodynamically more stable calcite form after being calcined at 300°C for 3 h, while the majority of the pearl shell powder was of the calcite form after being calcined at 600°C for 3 h. All of the calcium carbonate in the pearl shell powder was in the thermodynamically more stable calcite form after being calcined at 700°C for 3 h as shown in Scheme 1.

Examination of Figure 5 shows that there are no characteristic XRD peaks (such as 36.2, 38.0, and 39.6°) of both aragonite and calcite calcium carbonate for the pearl shell powder after being calcined at 900°C for 3 h, indicating that the calcium carbonate has been completely decomposed. These results also suggest that decomposition of the aragonite calcium carbonate was much quicker than the corresponding morphological transformation from the less stable aragonite into the thermodynamically more stable calcite. Decomposition of the calcite calcium carbonate is expected to be negligible at around 800–900°C since the decomposition temperature of calcite is 1330°C.[12]

Characterization of the layered biopolymer molecules

The biopolymer molecules of the pearl shell powder were monitored using IR spectroscopy. Figure 6 presents the IR spectra of variable pearl shell powders. Examination of Figure 6 shows a gradual decrease of the characteristic IR absorption peaks for the carboxyl (1808 cm^{-1}) and amine (2515 cm^{-1}) functional groups of proteins as the calcination temperature increases. Interestingly, the IR absorption peaks completely disappeared for the pearl shell powder calcined at 700, 800, or 900°C. In contrast, a strong characteristic IR absorption at 3640 cm^{-1} for calcium oxide (CaO) was observed for the pearl shell powder calcined at 800 or 900°C for 3 h. These observations provided the conclusive evidence that the layered biopolymer molecules completely

degraded at around 700°C and that calcium carbonate decomposed at around 800–900 °C.

It is worth noting that the characteristic IR absorbance peak at $\sim$ 1080 cm^{-1} for the CO_3^{2-} ions of the aragonite crystal[16] decreased with the calcination temperature from 150 to 300°C, and then completely disappeared for the pearl shell powder calcined at 600 or 700°C. These results are consistent with accelerated morphological transformation from the less thermodynamically stable aragonite into the more thermodynamically stable calcite as the calcination temperatures increased.

Optimization of the filler weight content for EP composites

When an object is impacted, a pressure gradient forms along the impacted direction from surface to bottom. The object will collapse around the relatively weaker area when the object cannot effectively disperse the impacted stress. It is well-known that incorporation of inorganic particulate filler into a polymer matrix can disperse the mechanical stress because of the interfacial interaction. Nanoparticle fillers are expected to be much more effective than conventional particles primarily due to the much larger ratios of particle surface area to volume (mass) for the nanoparticles. It is not surprising to find that the mechanical strength of the composite does not increase but rather decreases if the interfacial interactions between the filled particles with the polymer matrix molecules are poor.[17]

The impact strength of the EP composites was improved when incorporated with nanosized calcium carbonate particles.[18] Previously, we have also observed similar mechanical improvements for the EP composites when reinforced by other inorganic filler such as silica.[19,20] Since the mechanical performance of a particulate filled composite is highly
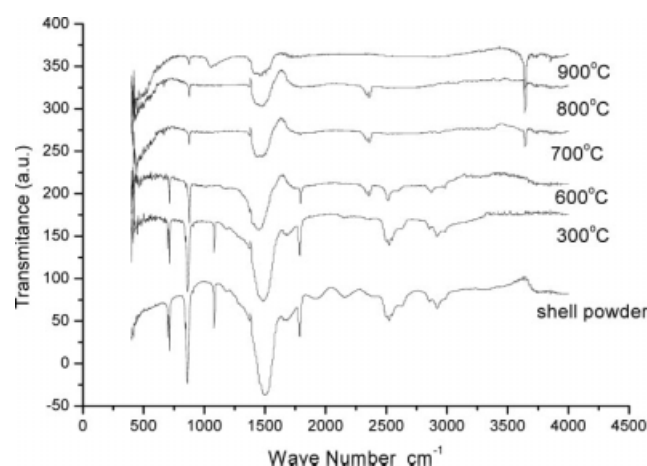

Figure 6 Infrared (IR) spectra of the uncalcined and calcined pearl shell powders.
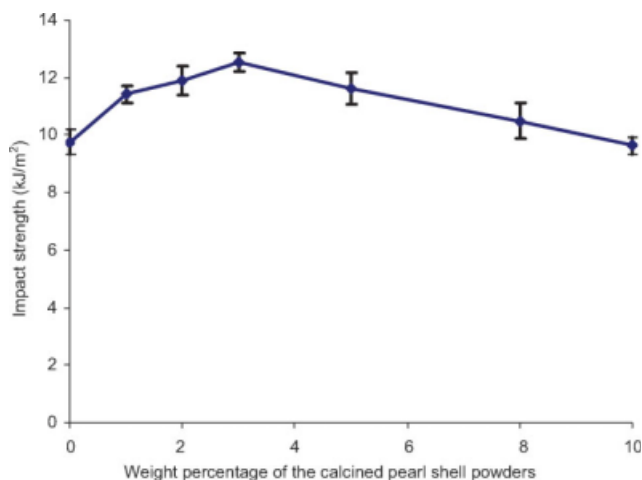
Figure 7 Dependence of the impact strength of the epoxy resin composites with the weight percentage of the pearl shell powder calcined at 200°C for 3 h. All impact strengths are expressed as an average ± SEM (standard error mean) for five measurements. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

dependent upon the amount of particulate filler,[18–20] the weight content of the calcined pearl shell powder was first optimized for the present study. For the optimization, a series of EP composites were prepared using 0–10% weight of the pearl shell powder calcined at 200°C. The impact strengths of the processed EP composites were determined and the related results are presented in Figure 7.

Examination of Figure 7 shows that the impact strength of the control EP is 9.7 ± 0.4 kJ/m^2, which is in agreement with 10.2 kJ/m^2 reported for a similar EP.[18] The impact strengths of the resulting EP composites increased with the weight content percentage up to 3.0% weight of the calcined pearl shell powder, indicating that the incorporated pearl shell powder and calcium carbonate have similar interfacial interactions with the surrounding matrix molecules although the layered biopolymers were not completely degraded for the pearl shell powder calcined at 200°C. In contrast, the impact strengths of the EP composites decreased when the weight content loading of the calcined pearl shell powder exceeded 3.0%. The higher weight content loading of the calcined pearl shell powder may have caused the aggregation of the filled pearl shell powder particles, which were detrimental to the mechanical strength of the EP composites.[21]

Impact strengths of EP composites incorporated with the pearl shell powders calcined at different temperatures

To assess the effects of various calcination temperatures on the mechanical strength, EP composites were prepared with the optimum 3.0% weight content of the calcined pearl shell powders. The impact strengths of the resultant EP composites along with the control were summarized in Figure 8. The P-values of the t-test demonstrated that the improvements in impact strength were significant ($P < 0.05$) for all EP composites compared to the control EP.

Examination of Figure 8 shows that the incorporation of the pearl shell powders calcined at 200, 300, 600, and 700°C improved the impact strength of the EP composites by 25, 34, 44, and 79%, respectively. The much larger improvement of the impact strength using the pearl shell powders calcined at 600 and 700°C can be attributed to the greater interfacial interactions between the filled particles and the surrounding EP matrix molecules because of their larger specific surface area (Table I). The largest improvement in impact strength was obtained for the EP composite prepared using the pearl shell powder calcined at 700°C. As shown in the earlier sections, the layered biopolymeric materials of the pearl shell powder were not completely degraded after being calcined at 600°C for 3 h. For example, the specific surface area (18.5 m^2/g) of the pearl shell powder calcined at 700°C was over two times larger than that (7.9 m^2/g) of the pearl shell powder calcined at 600°C. Furthermore, the SEM image of the EP composite incorporated with the pearl shell powder calcined at 700°C indicated that the filler particles were relatively uniformly distributed in the EP composites as shown in Figure 9.

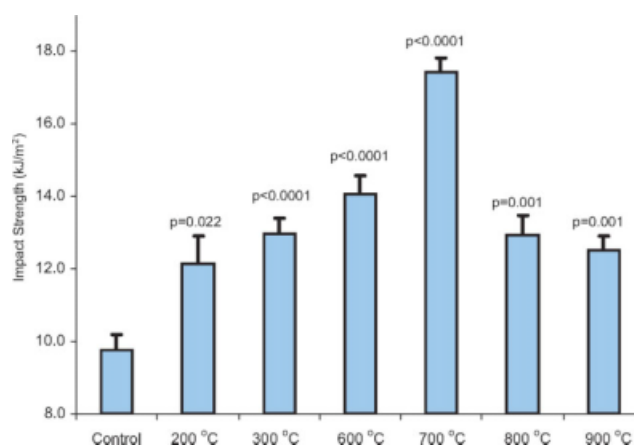Most intriguingly, the improvement of the impact strength (79%) for the EP composite incorporated

Figure 8 Dependence of the impact strength of the epoxy resin composites with the calcination temperatures of the pearl shell powders. All epoxy resin composites were prepared with 3% weight of the calcined pearl shell powders. Impact strengths are expressed as an average ± SEM (standard error mean) for five measurements. The P-values of the t-tests are also included. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]
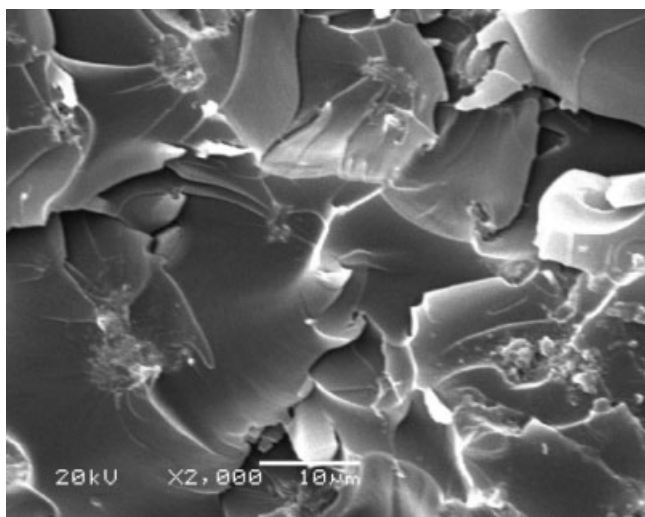
Figure 9 Scanning electron microscopy (SEM) image of the epoxy resin composite incorporated with the pearl shell powder calcined at 700°C for 3 h in the presence of the silane coupling agent.

with the pearl shell powder calcined at 700°C was found to be similar to that (70%) for the EP composites incorporated with the calcium carbonate nanoparticles.[18] The similar improvement may suggest that the calcined pearl shell powder and calcium carbonate nanoparticles had similar interfacial interactions with the surrounding EP matrix molecules. These results provide additional evidence that the pearl shell powder calcined at 700°C possesses the unique nanostructures.

EP composites prepared with calcium oxide

Although the specific surface areas of the pearl shell powders calcined at 800 and 900°C were even larger than that of the pearl shell powder calcined at 700°C (Table I), incorporation of the pearl shell powders calcined at 800 and 900°C only improved the impact strength of the composites by 34% and 29%, respectively, which were considerably smaller than the impact strength improvement (79%) by incorporation of the pearl shell powder calcined at 700°C.

As shown in earlier sections, the calcination of the pearl shell powders at 800 or 900°C not only completed the degradation of the biopolymeric materials, but also resulted in the decomposition of calcium carbonate into calcium oxide (lime). Thus, the lower mechanical strengths of the EP composites incorporated with the pearl shell powder calcined at 800 or 900°C must be associated with the relatively weaker interfacial interactions of the calcium oxide (lime) with the surrounding EP matrix molecules.[22] The morphological nanostructure of the resultant calcium oxide was expected to be similar to that of calcium carbonate as no change of the shape or size was

observed during the thermal decomposition of calcium carbonate into calcium oxide.[23] In other words, calcium carbonate is more effective than calcium oxide as inorganic filler for reinforcing the EP composites.

Effects of silane coupling agent

Silanes are well-known for their abilities to enhance adhesion of organic polymer matrix to inorganic substrate[24] and/or incorporated inorganic particles.[25] If the mechanical strength improvement by incorporation of the calcined pearl shell powder was caused by enhancement of the interfacial interactions of the filled particles with EP matrix molecules, then the impact strength should decrease for the EP composites prepared without the addition of the silane coupling agent. To test this hypothesis, EP composites were prepared following the same protocol except for the addition of the silane coupling agent. The impact strengths of these EP composites together with those with the silane coupling agent were all summarized in Figure 10 for comparison.

Examination of Figure 10 shows that the EP composites prepared without the silane coupling agent have considerably smaller impact strengths than those prepared with the silane coupling agent, indicating that the silane coupling agent is essential for preparation of the calcined pearl shell powder-filled EP composites. The SEM image of the EP composite without the silane coupling agent is shown in Figure 11. It is clear that the pearl shell powder was more uniformly distributed in Figure 9 than in Figure 11, suggesting that the silane coupling agent also
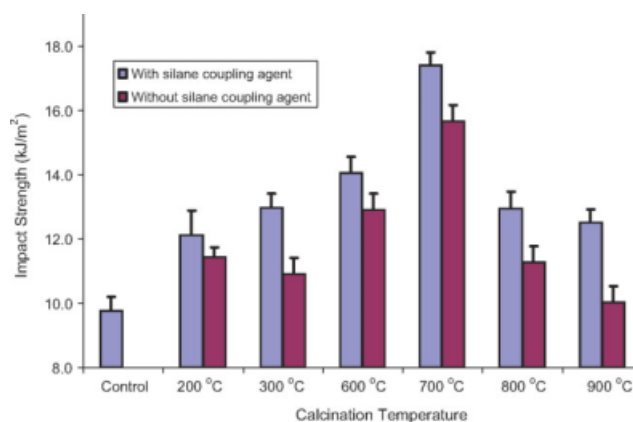

Figure 10 Comparison of the impact strength of the epoxy resin composites prepared in the presence and absence of the silane coupling agent. All epoxy resin composites were prepared with 3% weight of the pearl shell powders. Impact strengths are expressed as an average ± SEM (standard error mean) for five measurements. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
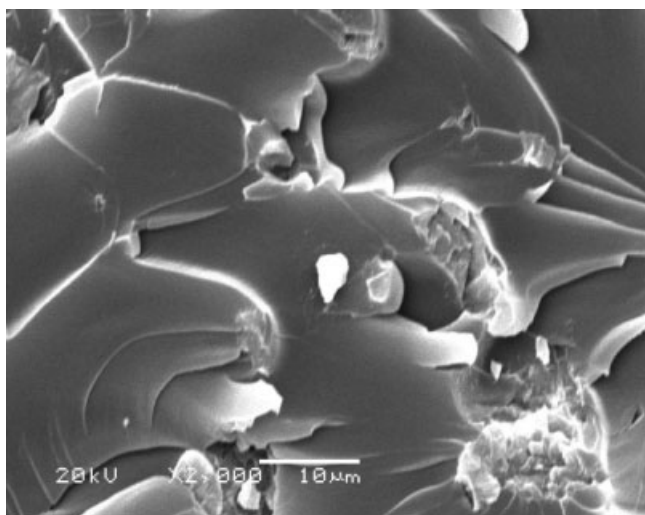
Figure 11 Scanning electron microscopy (SEM) image of the epoxy resin composite incorporated the pearl shell powders calcined at 700°C for 3 h in the absence of the silane coupling agent.

improved the dispersion of the pearl shell powder in the EP composites.

Calcium carbonate with sponge-like nanostructure

The fascinating applications of nanotechnology have been the impetus for the field's rapid development in the past few decades.[26] Nanomaterials have demonstrated many unique electronic and optical properties since the nanoparticle size is in the realm where quantum effects predominate instead of the classical physical laws for bulk materials.[27]

Calcium carbonate nanoparticles are biodegradable and are much more environmentally friendly than silica nanoparticles. While silica nanoparticles have been produced at a megaton scale,[28] it has been difficult to produce calcium carbonate nanoparticles. Mechanical grinding is impractical for producing calcium carbonate nanoparticles as the process yields densely agglomerated particles.[29] Currently, a majority of the calcium carbonate nanoparticles are synthesized from wet chemical reactions such as calcium hydroxide with carbon dioxide or calcium chloride with sodium carbonate.[14] However, the wet chemical method has the drawbacks of a relatively large particle size distribution and propensity for contamination by the precursor chemicals.[30] Recently, a flame spray process was reported to synthesize calcium carbonate nanoparticles from calcium 2-ethylhexanoate in a methane-oxygen-flame, but this complicated gas-phase process is expected to be difficult to scale up for industrial applications.[31]

It is apparent that the calcination approach for the preparation of the sponge-like nanostructured calcium carbonate can be readily scaled up for industrial applications. In addition, the calcination method has advantages over traditional methods, mainly lower production cost, environmental friendliness, etc. Furthermore, the calcium carbonate derived from the calcination method has a unique sponge-like porous nanostructure, which is different with the spherical nanoparticles prepared from the traditional methods such as the wet chemical reactions.[14] Moreover, the calcination method should also be applicable to other biomineral wastes such as sea shells, egg shells, etc.

CONCLUSIONS

The layered biopolymeric materials of the pearl shell powder were completely degraded after being calcined at around 700°C for 3 h, resulting in sponge-like porous calcium carbonate powder. The nanostructure of the porous sponge-like calcium carbonate nanoparticles is different with the spherical calcium carbonate nanoparticles prepared from the literature methods.[14] This simple calcination approach will have broad industrial applications as it utilizes the potentially envionmentally harmful pearl shell waste to produce useful calcium carbonate with porous nanostructures.

EP composites prepared using the calcined pearl shell powders demonstrsted that the calcined pearl shell powders were effective inorganic filler materials (with respect to cost and performance) for improving the impact strength of EP composites. The EP composites were found to have the highest impact strength improvement when contained 3% weight content of the calcined pearl shell powder. The largest impact strength improvement has been obtained for the EP composite prepared using the pearl shell powder after being calcined at 700°C for 3 h. Higher improvement of the impact strength was obtained for the EP composites prepared with the silane coupling agent than those prepared without the silane coupling reagent.

References

1. May, C. A., Ed. Epoxy Resins, Chemistry and Technology, 2nd ed.; Maecel Dekker: New York, 1988.
2. Ratna, D. Epoxy Composites: Impact Resistance and Flame Retardancy; Smithers Rapra Technology; Shawbury, UK, 2005; Vol. 16.
3. Sui, G.; Jana, S.; Salehi-Khojin, A.; Neema, S.; Zhong, W. H.; Chen, H.; Huo, Q. J Appl Polym Sci 2008, 109, 247.
4. Mishra, S.; Shimpi, N. G. J Appl Polym Sci 2005, 98, 2563.
5. Currey, J. D. Proc R Soc London Ser B 1941, 196, 443.
6. Aksay, I. A.; Trau, M.; Manne, S.; Honma, I.; Yao, N.; Zhou, L.; Fenter, P.; Eisenberger, P. E.; Gruner, S. M. Science 1996, 273, 892.
7. Fritz, M.; Belcher, A. M.; Radmacher, M.; Walters, D. A.; Hansma, P. K.; Stucky, G. D.; Morse, D. E.; Mann, S. Nature 1994, 371, 49.
8. Weiner, S.; Traub, W.; Parker, S. B. Phil Trans R Soc B 1984, 304, 425.

9. Jackson, A. P.; Vincent, J. F. V.; Turner, R. M. Proc R Soc London Ser B 1988, 234, 415.

10. Tang, W.; Wang, C.; Chen, D. Polym Degrad Stab 2004, 87, 389.

11. Sakanishi, K.; Ikeyama, N.; Sakaki, T.; Shibata, M.; Miki, T. Ind Eng Chem Res 1999, 38, 2177.

12. Lide, D. R. CRC Handbook of Chemistry and Physics; 79th ed.; CRC Press: Boca Raton, Florida, 1999; p 4.

13. Nakamura, Y.; Yamaguchi, M.; Okubo, M.; Matsumoto, T. J Appl Polym Sci 1992, 45, 1281.

14. He, M.; Forssberg, E.; Wang, Y.; Han, Y. Chem Eng Commun 2005, 192, 1468.

15. Wolf, G.; Gunther, C. J Therm Anal Cal 2001, 65, 687.

16. Ning, Y. Structural Identification of Organic Compounds and Organic Spectroscopy, 2nd ed.; Science Press: Beijing, China, 2001.

17. Nicolais, L.; Narkis, M. Polym Eng Sci 1971, 11, 194.

18. Li, L.; Zou, H.; Shao, L.; Wang, G.; Chen, J. J Mater Sci 2005, 40, 1297.

19. Zeng, M.; Sun, X.; Yao, X.; Ji, G.; Chen, N.; Wang, B.; Qi, C. J Appl Polym Sci 2007, 106, 1347.

20. Zhu, J. B.; Yang, X. J.; Cui, Z. D.; Zhu, S. L.; Wei, Q. J Macromol Sci B 2006, 45, 811.

21. Rong, M. Z.; Zhang, M. Q.; Zheng, Y. X.; Zeng, H. M.; Walter, R.; Friedrich, K. Polymer 2001, 42, 167.

22. Bikerman, J. J. Ind Eng Chem 1967, 59, 40.

23. Wu, C.-M.; Lin, C. I. J Chem Eng Jpn 2005, 38, 734.

24. Mittal, K. L., Ed. Silanes and Other Coupling Agents; VSP: Zeist, The Netherlands, 1992.

25. Fowkes, F. M.; Dwight, D. W.; Cole, D. A. J Non-Cryst Solids 1990, 120, 47.

26. Malsch, N. H., Ed. Biomedical Nanotechnology, Taylor & Francis: New York, 2005.

27. Schmid, G., Ed. Nanoparticles from Theory to Application, Wiley-VCH Verlag: Weinheim, 2004.

28. Stark, W. J.; Pratsinis, S. E. Powder Technol 2002, 126, 103.

29. Willert, M.; Rothe, R.; Landfester, K.; Antonietti, M. Chem Mater 2001, 13, 4681.

30. Gomez-Morales, J.; Torrent-Burgues, J.; Rodriguez-Clemente, R. J Cryst Growth 1996, 169, 331.

31. Huber, M.; Stark, W. J.; Loher, S.; Maciejewski, M.; Krumeichb, F.; Baikera, A. Chem Commun 2005, 648.