

Fire-Retardant Plastic Material from Oyster-Shell Powder and Recycled Polyethylene

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ABSTRACT: A series of plastic materials from recycled polyethylene (PE) and oyster-shell powder were prepared to test their fire-retardant properties with an aim of finding a practical way of waste recycling. Oyster-shell powder was found to be mainly composed of calcium carbonate and it decomposed to calcium oxide and carbon dioxide at temperature higher than $\sim 800^\circ\text{C}$, thus preventing fire from access of oxygen by the produced carbon dioxide. This fire-retardation mechanism is environmental-friendly, since another available method, the inclusion of halogen-containing

compounds, normally generates toxic chemicals like dioxine during incineration. To improve mechanical properties of this composite material, surface of oyster-shell powder was coated with cetyltrimethylammonium bromide (CTAB). Flame retardation and the mechanical properties of these composite resins were analyzed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1583–1589, 2006

Key words: fire retardant; oyster shell; polyethylene; composite

INTRODUCTION

Enormous amount of waste polyethylene (PE) and polypropylene (PP) needs to be handled worldwide. Another waste product, oyster-shell powder, produced from the oyster nursery located along the southern coastline of Korea (annual production of the waste oyster shell in Korea is 250,000 tons) also needs special attention for its disposal.^{1,2} Therefore, it is highly desirable to device plastic materials that combine the above two waste products, for special purposes. Korea is one of the largest producers of cultivated oyster, with annual production $>300,000$ tons in the year 2003. Oyster-growing facilities count more than 475 and cover more than 3586 ha of area.^{3,4} Increase in oyster crop, however, resulted in the accumulation of waste oyster shell. Presently, major usage of waste shell includes fertilizer and oyster cultivation medium, but half the amount of the waste oyster shell is still not recycled, causing environmental hazard and scarcity of lot for storage. Thus, an innovative method of recycling the waste shell has to be designed to resolve the aforementioned problems. Oyster shell (mainly composed of CaCO_3) decomposes to CaO and CO_2 when heated above 800°C , and the generated CO_2 can extinguish fire by preventing the access of oxygen.⁵ Fire-retardant polymeric material has been

widely researched in the field of textile, composite, thermally insulating polyurethane, coating, molding, and so on.^{6–12} Utilizing the simple principle, fire-retardant plastics from oyster-shell powder and recycled PE were tested, according to the UL 94 specification. Flammability test results together with mechanical properties are discussed, and a method to improve mechanical properties is introduced.

EXPERIMENTAL

Materials and method

Recycled PE was obtained from the Korea Recycling Agency, and LDPE (HY5321) was from Hanhwa Chemical, Korea. Two grades of oyster-shell powder with different particle size were purchased from Hae Sung Limited, Korea, and the particle sizes were determined by Malvern Mastersizer particle-size analyzer. Elementary analysis confirmed that shell powder is mainly composed of CaCO_3 , since the measured carbon content (10%) is very close to its theoretical content (12%). Table I shows the elementary analysis results of shell powder. TGA and DTA thermograms were obtained by Scinco thermal analyzer (TGA S-1500 for TGA and STA S-1500 for DTA). Shell powder, after washing with double distilled water (1 L of distilled water for 1 kg of shell powder), was filtered and dried (150°C) before compounding.

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TABLE I
Elemental Analysis of Oyster Shell

| Sample | Elements | | | | |
|--------------|----------|-------|-------|-------|-------|
| | N | C | S | H | O |
| Oyster shell | 0.180 | 9.991 | 0.599 | 0.599 | 26.79 |

Compounding of composite material

Master batch (MB) of recycled PE containing 40 wt % of shell powder was made with twin-screw extruder (Bau Tech model BA-19, $\phi = 20$ mm), and additional specimens containing 10, 20, or 30 wt % of shell powder were prepared from the 40 wt % MB. The temperature profile was kept at 180°C at the feeder zone, and 200°C at the melting and metering zone. Mechanical and flammability test specimens were prepared using a Mini-Max molder (Bau Tech model BA-915).

Flammability testing

Flammability test was conducted by 20 mm vertical burning test method described in UL 94 specification.¹³ Standard bar specimen has 125 mm length, 13.0 mm width, and 3.0 mm thickness. From flammability test, t_1 , t_2 , and t_3 were obtained, where t_1 is after-flame time after first flame application, t_2 is after-flame time after second flame application, and t_3 is after-glow time after second flame application. As shown in Figure 1, specimen is exposed to the flame front for 10 s, and then removed from the flame. First, the time for which the flame is on the specimens (t_1) was measured. After 5 s after the first flame extinguished, the flame was applied to the specimen for another 10 s, and then removed. The time for which the flame is on the specimen (t_2) was measured. After the flame extinguished, the time until the final glow on the specimen disappeared (t_3) was measured. Specific flame time requirements for each classification are summarized in Table II.

Surface modification

Shell powder was coated with cetyltrimethylammonium bromide (CTAB) by stirring in 1 mM aqueous CTAB solution for a day, and recovered after filtration and drying. Surface loading of CTAB checked by elemental analysis of nitrogen of shell powder was about 0.1 mmol/g.

Mechanical properties

Tensile strength was measured according to ASTM D-638 by UTM (Lloyd Instrument, model LR50K) with a dumbbell-type specimen under the following conditions: gauge length = 25 mm; crosshead speed = 10

mm/min; and load cell = 2.5 kN. Notched Izod impact strength was measured by impact tester (Testing Machine Inc., Model TMI 43-02, pendulum 75 kg/cm) according to ASTM D-256. At least five specimens were tested and the average value was used for the data plot. Flexural and compressive strength were also tested according to ASTM D-790 and D-695, respectively, using UTM (Lloyd Instrument, model LR50K), and the average values were used for the data plot.

Heat deflection temperature measurement

Heat deflection temperature (HDT) was measured according to ASTM D-648, using an ATS Farr HDT-VICAT tester MP/3. Specimens were exposed to the constant load with a heating rate of 2°C/min, and the temperature at which the specimens were deformed to 0.25 mm was determined as the HDT.

RESULTS AND DISCUSSION

Elemental analysis confirmed that calcium carbonate is the major component of the shell. However, we are very curious about the exact calcium carbonate content of the shell, because the success of shell powder being a fire retardant depends heavily on the amount of evolved CO₂ from the shell powder. Shell powder is classified into two grades (fine and coarse). Both grades with different CaCO₃ content were thermogravimetrically analyzed by TGA: the CaCO₃ contents (calculated from the weight loss of CO₂ around 770°C at which temperature 44% of weight loss was that of pure CaCO₃ and CaCO₃ content was determined by

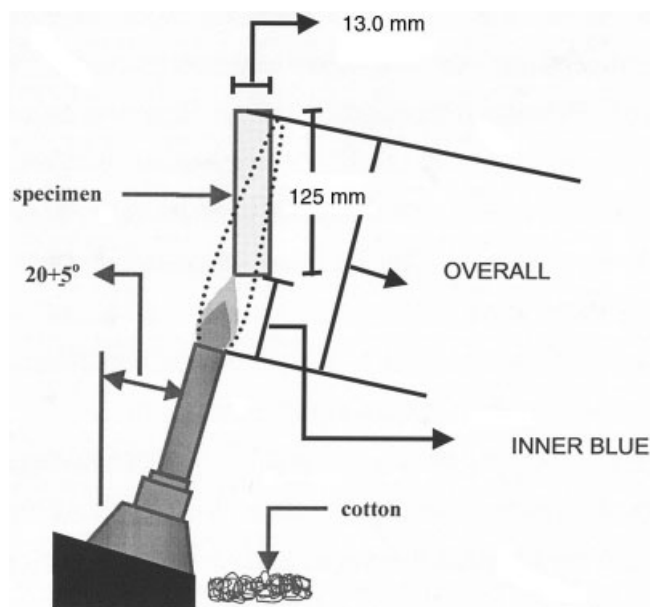


Figure 1 Schematic of flammability test apparatus assembled according to UL 94 specification.

TABLE II
UL 94 Specification of Fire-Retardant Plastic

| Test area | V-0 (s) | V-1 (s) | V-2 (s) |
|--|---------|---------|---------|
| After-flame time (t_1 or t_2) | ≤10 | ≤30 | 30 |
| Total after-flame time ($t_1 + t_2$) | ≤50 | ≤250 | ≤250 |
| After-flame plus afterglow time ($t_2 + t_3$) | ≤30 | ≤60 | ≤60 |
| After-flame or afterglow of any specimen up to the holding clamp | No | No | No |
| Cotton indicator ignited by flaming particles or drops | No | No | Yes |

dividing weight loss percentage by 44%) were found to be 93.8% (41.3/44.0) for the fine powder and 74.5% (32.8/44.0) for the coarse one. TGA thermogram of coarse shell powder showed sharp drop in weight around 770°C (Fig. 2).

Average particle size of the fine powder (3–5 μm) was much smaller than that of the coarse one (10–15 μm); smaller particle size was advantageous in homogeneous compounding with PE resin and generate more CO_2 due to higher surface area. DTA analysis also showed a sharp transition peak at 771.9°C corresponding to decomposition of CaCO_3 (Fig. 3). Combining the aforementioned results, fine-grade powder was selected for the rest of the experiments.

Three factors were varied in compounding: shell powder content was varied in series (10, 20, 30, and 40 wt %); the used PE resin was virgin LDPE or recycled PE; surface of shell powder was coated with CTAB to improve the compatibility between resin and shell powder. Therefore, 12 different kinds of composite PE resin were prepared for testing (four different shell contents of recycled PE, four different shell contents of recycled PE, and four different shell contents of virgin LDPE with CTAB-coated shell powder). Maximum

stress of the above specimens were compared: maximum stress of LDPE specimen decreased with the increase in shell content, for 10 wt % shell, and however, remained changeless beyond this. Meanwhile, recycled PE specimens more or less maintained constant strength for the entire cases of shell content; interestingly enough, recycled PE with CTAB-coated shell powder also showed similar behavior with the recycled PE (Fig. 4). It is not uncommon that mechanical properties of plastic material decrease with the inclusion of inorganic particle that hinders organized packing of polymer chains, explaining the decrease in LDPE case. Recycled PE, composed of LDPE and HDPE, generally showed higher maximum stress than other compared PEs, because HDPE was superior to LDPE in mechanical properties. However, the unknown content of HDPE in recycled PE and the decrease in mechanical property during recycling process were, presumably, responsible for the comparable maximum stress results of both recycled PE and LDPE. Surface coating of shell powder with cationic surfactant, CTAB, reduced the surface polarity and should lead to compatible mixing of shell powder with recycled PE resin. However, in this case, recycled

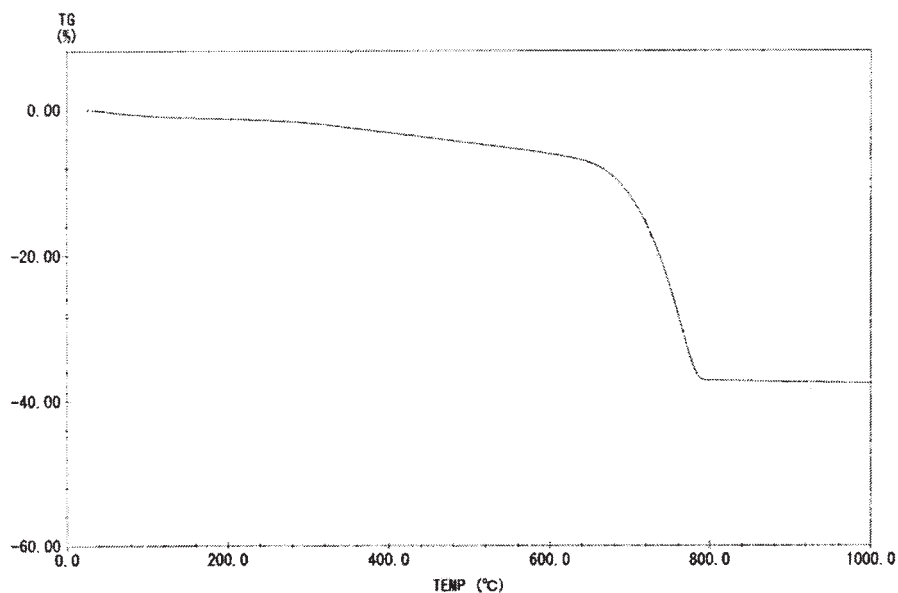


Figure 2 TGA profile of shell powder.

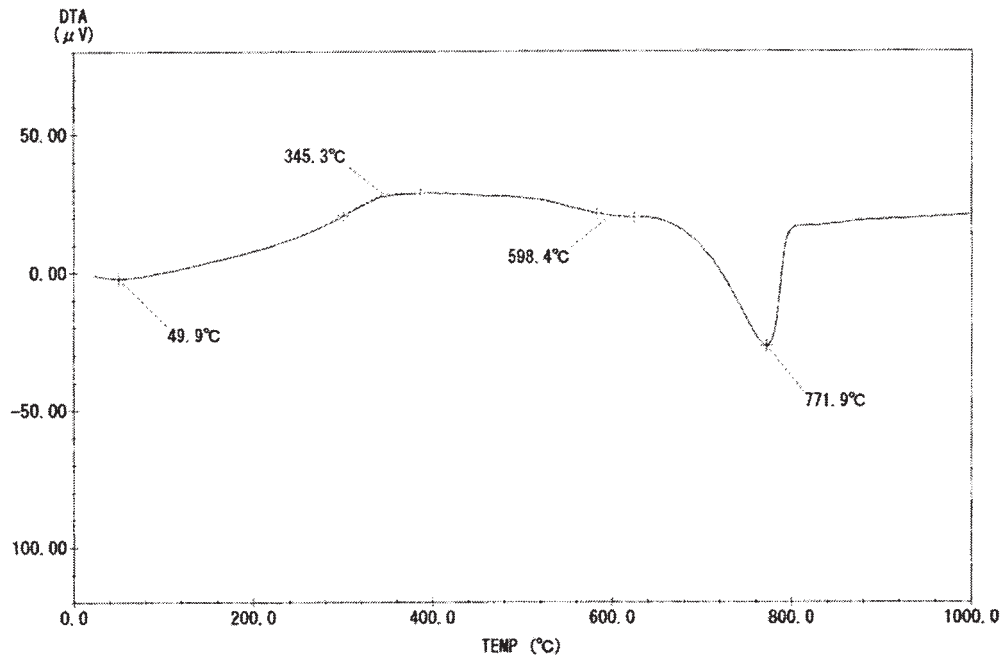


Figure 3 DTA profile of shell powder.

PE with no surface coated shell showed slightly better or similar maximum stress, depending on the shell content. Therefore, surface coating method can partially make up the general problem of maximum stress decrease, when inorganic and organic materials are compounded together.

Strain-at-break of the specimens generally decreased in strain values with higher shell content (Fig. 5). LDPE was inferior to recycled PEs in terms of absolute strain-at-break values; however, these discrepancies decreased generally with the increasing shell content. However, CTAB-coated recycled PE showed interesting behavior this time; in this case, it

exhibited highest strain-at-break values compared to recycled PE with no CTAB-treated shell. This indicates the increased interfacial bonding between the CTAB-coated shell and the recycled PE matrix.

Notched Izod impact strength also increased slightly for 10 wt % shell, and then, decreased with shell content for all of the specimens (Fig. 6): LDPE has the lowest and recycled PE with coated shell has the highest impact strength. Meanwhile, recycled PE with no CTAB-treated shell showed slightly lower impact strength for the intermediate shell content, but became slightly higher for >30 wt % shell.

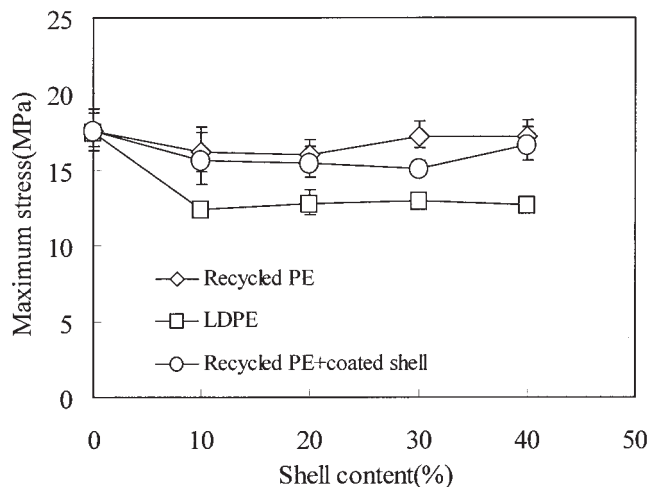


Figure 4 Maximum stress versus shell content profile of various PEs.

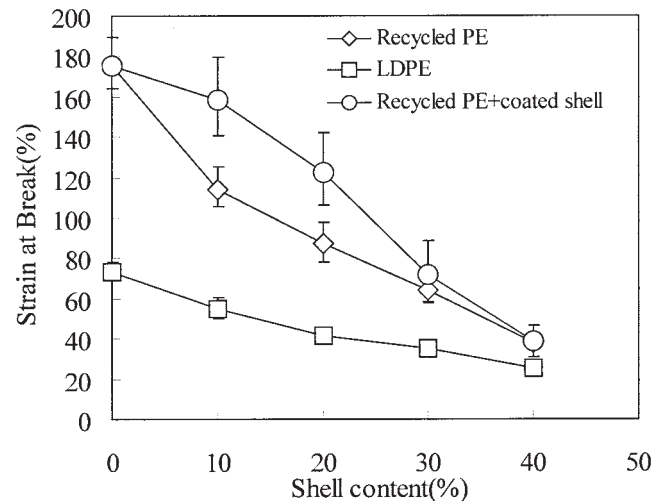


Figure 5 Strain-at-break versus shell content profile of various PEs.

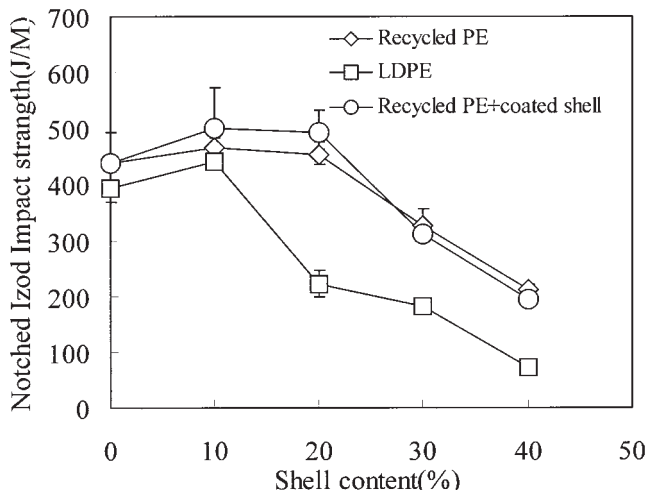


Figure 6 Notched Izod impact strength versus shell content profile of various PEs.

The similarity of recycled PE and CTAB-coated recycled PE in HDT was quite contrasting to LDPE with generally lower HDT value, suggesting that the existing HDPE in the recycled PE matrix accounted for this behavior (Fig. 7).

Flexural and compressive strength of the PEs were compared in Figures 8 and 9. As can be seen from the overall increase in flexural and compressive strength with shell content, inclusion of shell powder in PE, compared with the above mechanical properties that tested elongation strength, improved the PEs strength in withstanding external flexural and compressive stress. Especially, CTAB coating was very effective in additionally increasing flexural and compressive strength, suggesting that surface coating of inorganic particle worked better in compressive mode than in elongation one.

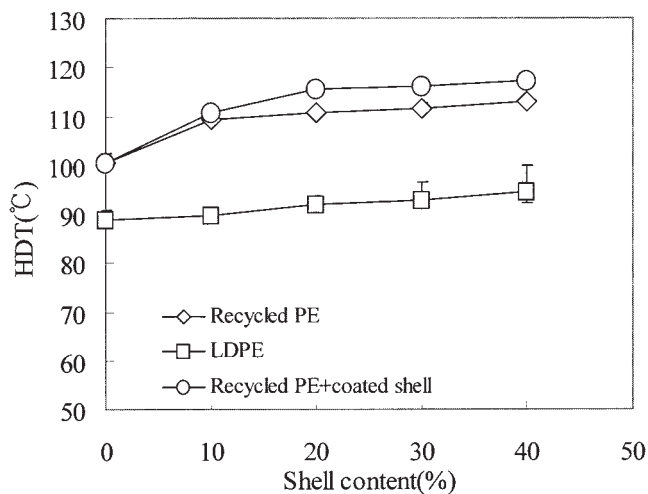


Figure 7 HDT versus shell content profile of various PEs.

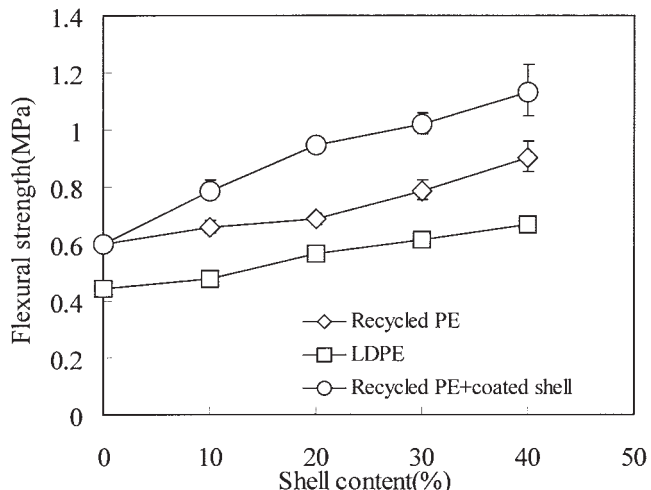


Figure 8 Flexural strength versus shell content profile of various PEs.

Surfaces of impact-fractured (a) recycled PE and (b) CTAB-coated recycled PE with 20 wt % of shell content were scanned by SEM (Fig. 10). Figure 10(a) shows uneven distribution of shell powder, while Figure 10(b) shows more even distribution of the CTAB coated powders, indicating the effect of increased interfacial bonding of the CTAB between the shell and recycled PE matrix. Also the fracture surface of recycled PE with CTAB-coated shell showed more plastic deformation than that of recycled PE with no CTAB-coated shell.

Flammability test results of shell-containing PEs are summarized in Table III. Virgin LDPE and recycled PE with 10 wt % shell completely burned out at first flame application.

Also, the recycled PE with no CTAB-treated shell at more than 20 wt % completely burned out at second

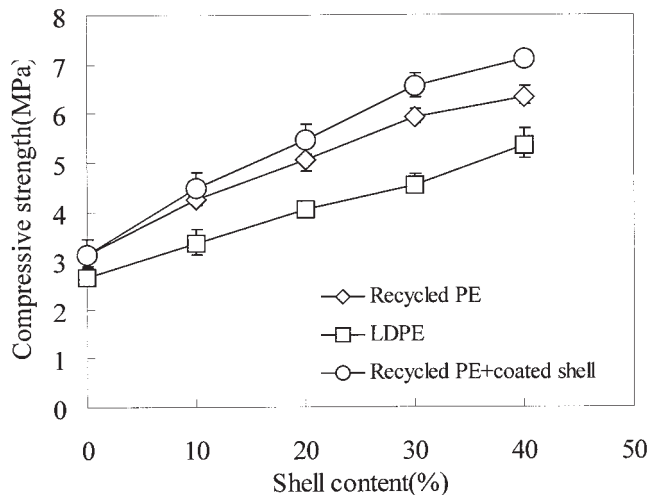
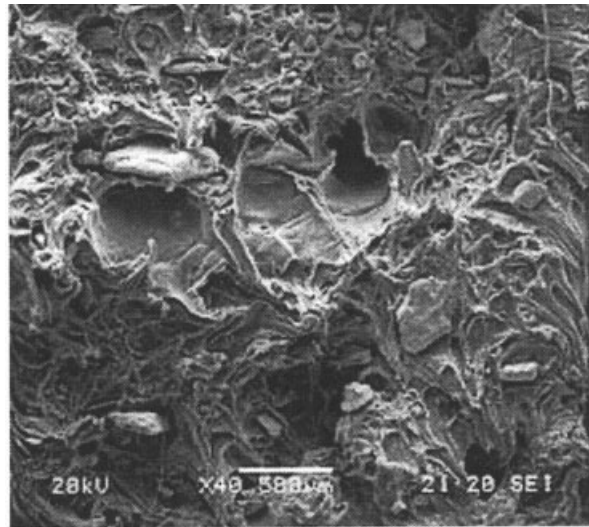
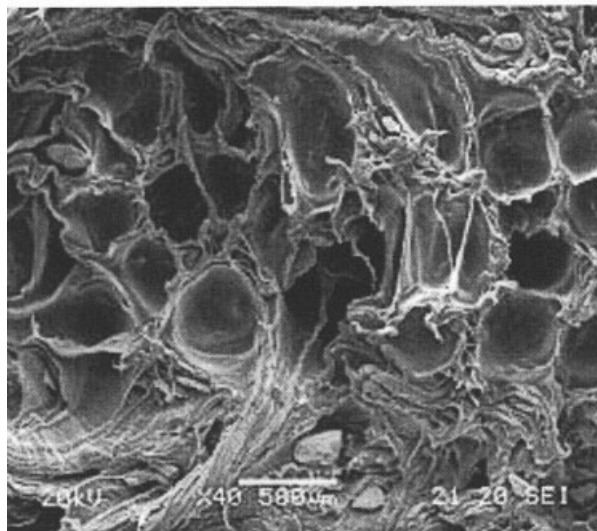


Figure 9 Compressive strength versus shell content profile of various PEs.



(a)



(b)

Figure 10 SEM image of fractured surface of recycled PE with (a) shell and (b) CTAB-coated shell.

flame application. However, recycled PE with CTAB-coated specimens showed quite improved flame retardancy compared to uncoated shell. For example, inclusion of 30 wt % of CTAB-coated shell exhibited V-0 classification, according to UL 94 specification. This is attributed to the more even dispersion of the CTAB-treated shell powder compared to untreated shell. This evenly dispersed CTAB-coated shell powder provided a larger external surface of the shell compared to the no CTAB coated shell, and resulted in a higher CO₂ evaporation during the flammability test.

Flammability tested specimens in Figure 11 demonstrated that the original shape could be maintained as the shell content increased. Overall, the fact that sur-

TABLE III
Flammability Test Results of the Oyster-Shell Containing Polyethylene Specimens

| Resin | t_1 | t_2 | t_3 |
|--|------------|------------|-------|
| LDPE | 2 min 10 s | — | — |
| Recycled PE + 10 wt % shell ^a | 3 min 10 s | — | — |
| Recycled PE + 20 wt % shell ^a | 1 s | 3 min 40 s | — |
| Recycled PE + 30 wt % shell ^a | 2 s | 3 min 50 s | — |
| Recycled PE + 40 wt % shell ^a | 1 s | 3 min 50 s | — |
| Recycled PE + 10 wt % shell ^b | 2 s | 3 min 10 s | — |
| Recycled PE + 20 wt % shell ^b | 2 s | 3 min 15 s | — |
| Recycled PE + 30 wt % shell ^b | 2 s | 1 s | 0 s |
| Recycled PE + 40 wt % shell ^b | 1 s | 1 s | 0 s |

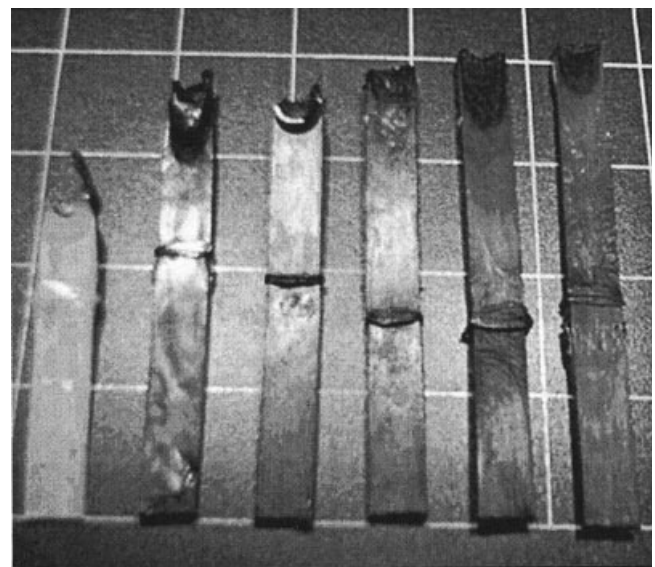
^a Normal shell.

^b CTAB-coated shell.

face coating of shell powder with CTAB improved the mechanical properties as well as flammability, and recycled PE with CTAB-coated shell content higher than 30 wt % could meet V-0 requirement encouraged us in developing fire-retardant plastic from waste materials.

CONCLUSIONS

Fire-retardant plastics were prepared from recycled PE and oyster shell-powder that was coated with cationic surfactant, to increase compatibility with PE. Shell powder was mainly composed of CaCO₃, and the fire-retardation mechanism depended on the car-



(a) (b) (c) (d) (e) (f)

Figure 11 Comparison of flame-tested specimens: (a) LDPE, (b) recycled PE, (c) recycled PE with 10 wt % of shell content, (d) recycled PE with 20 wt % of shell content, (e) recycled PE with 30 wt % of shell content, and (f) recycled PE with 40 wt % of shell content.

bon dioxide that generated at temperature higher than 800°C. Recycled PE generally showed better mechanical properties than LDPE, but CTAB-coated shell powder improved the mechanical properties, such as strain-at-break, impact strength, compressive, and flexural strengths compared with recycled PE with no CTAB coated shell. Recycled PE with CTAB-coated shell content higher than 30 wt % could be classified as V-0 grade, according to UL 94 specification. Environment-friendly fire-retardant plastic that liberates nothing harmful to surrounding can be prepared from waste materials.

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