

# Synthesis and Tensile Properties of a Novel Composite of *Chlorella* and Polyethylene

Toshi Otsuki,<sup>1</sup> Farao Zhang,<sup>2</sup> Hiroshi Kabeya,<sup>2</sup> and Takahiro Hirotsu<sup>2</sup>

<sup>1</sup>Ishikawajima-Harima Heavy Industries Company, Ltd., 1 Shin-Nakahara-cho, Isogo-ku, Yokohama 235-8501, Japan

<sup>2</sup>National Institute of Advanced Industrial Science and Technology, 2217-14 Hayashi-cho, Takamatsu 761-0395, Japan

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**ABSTRACT:** A novel composite of the green microalga *Chlorella* sp. with polyethylene (PE) was synthesized through chemical modification of PE with maleic anhydride (MA), with respect to the biological fixation of CO<sub>2</sub> with *Chlorella* sp. The interaction of *Chlorella* grains with a PE matrix is strikingly enhanced by the chemical modification of PE with MA. The tensile strength of a *Chlorella*-MA-modified PE composite (Ch-MPE) with a *Chlorella* content of 40 wt % is more than 2 times greater than that of a composite derived from unmodified PE. The marked increase in tensile

strength is attributed to the formation of chemical bonds between *Chlorella* grains and the PE matrix, from IR and SEM studies. Because of the satisfactory thermal plasticity of Ch-MPE, it can be easily shaped into plate and dishlike moldings by a heat-pressurizing method. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 812–816, 2004

**Key words:** *Chlorella*; maleic anhydride; polyethylene (PE); composites; tensile properties

## INTRODUCTION

Biological fixation of CO<sub>2</sub> by use of a photosynthetic microalga such as *Chlorella* sp. has been considered a promising method for decreasing CO<sub>2</sub> in the atmosphere<sup>1</sup> because of a high utilization rate (10–20%) of light energy with *Chlorella* compared to that with common plants (0.1–0.5%). To make such a fixation system practical, it is important to make effective use of the microalgae after biological fixation of CO<sub>2</sub>. Thus, we focused our interest on the use of *Chlorella* as a filler in thermoplastics such as polyethylene (PE)<sup>2</sup> with a view toward their application as building materials.

Because of the lack of affinity of *Chlorella* for PE, compounding of *Chlorella* with PE requires chemical modification of PE so that the modified PE can then interact strongly with *Chlorella* through chemical bonds between them. Maleic anhydride (MA) has been reported to be an effective modifier for PE<sup>3</sup> and polypropylene.<sup>4</sup> In this study, we describe the synthesis and tensile properties of a novel composite of *Chlorella* and PE characterized by chemical modification of PE with MA in a solid phase.

## EXPERIMENTAL

### Materials

*Chlorella* (Yaeyama Shokusan, Japan) was spray-dried after centrifugal concentration. PE (high density, MW  $\cong$  40,000; Mitsui Sekiyu Kagaku, Japan) was mechanically pulverized into spherical grains (size  $\sim$  1 mm) before use. The other commercial-grade reagents were used without further purification.

### Synthesis

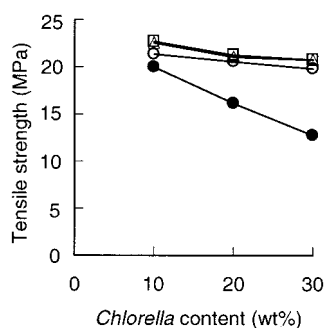
Chemical modification of PE and preparation of a *Chlorella*-PE composite were investigated in a roller mixer with a chamber volume of 60 cm<sup>3</sup> by the following two procedures.

#### Procedure 1

1. An acetone solution of 40 wt % MA and 2 wt % benzoyl peroxide (BPO) was sprayed onto PE powder and well blended [MA : BPO : PE (in weight) = 5.0 : 0.25 : 100].
2. After feeding into a roller mixer, the mixture was melt-mixed at 160°C for 20 min to obtain MA-modified PE (MPE).
3. The cooled MPE was shaped into pellets (size = 1 mm).
4. MPE pellets were melt-mixed with PE powder at 160°C for 7.5 min.

Correspondence to: T. Hirotsu (takahiro-hirotsu@aist.go.jp).

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**Figure 1** Effects of MPE amount on tensile strength values of *Chlorella*-MPE composites with constant MPE/Ch ratios: 0 (●), 1/4 (○), 2/4 (△), and 3/4 (□).

- Chlorella* was fed into the melted mixture of MPE and PE and treated at 160°C for 7.5 min to obtain a *Chlorella*-PE composite.

#### Procedure 2

- An acetone solution of 20 wt % MA and 1 wt % BPO was sprayed onto PE powder and well blended [MA : BPO : PE (in weight) = 0.25 : 0.012 : 100].
- After feeding into a roller mixer, the mixture was melt-mixed at 160°C for 30 min for preparation of MPE.
- Chlorella* was directly fed into the melted MPE and treated at 160°C for 10 min to obtain a *Chlorella*-PE composite.

Both composites were shaped into pellets with a size of less than 3.36 mm.

#### Tensile properties

Test sheet samples of the composites were prepared by heat-pressurizing the pellets (160°C, 2.2 MPa, 2 min) and were conditioned at 20°C and 65% relative humidity in an environmental chamber for 24 h. The tensile properties of the conditioned samples were measured with a tensile tester according to the testing method for tensile properties of plastics (at a strain speed of 50 mm/min).<sup>5</sup>

#### Moldings

A plate of the composite [size: 15 cm × 15 cm × 3–5 mm (width × length × thickness)] was obtained by heat-pressurizing 150 g of the pellets in an aluminum mold of a rectangular shape at 160°C and 2.2 MPa for 10 min. A dish-type molding was prepared by heat-pressurizing 15 g of the pellets in a stainless-steel mold [size: 10 cm × 6 cm × 1.5 cm (upper diameter

× bottom diameter × height)] at 150°C and 2.2 MPa for 20 min.

#### Other measurements

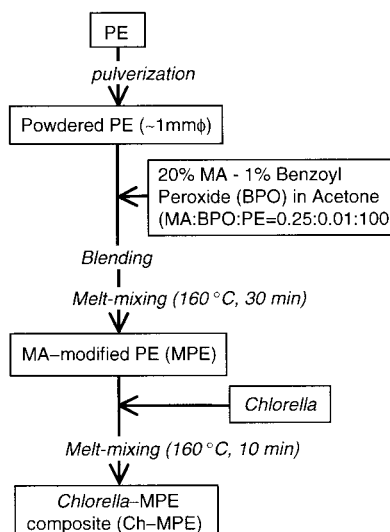
Microstructures of fractures of the composites were observed with an S-2460N scanning electron microscope (SEM; Hitachi, Osaka, Japan), and the FTIR spectra of *Chlorella*, MPE, and the composite were obtained with a Perkin-Elmer model Spectrum 2000 spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

## RESULTS AND DISCUSSION

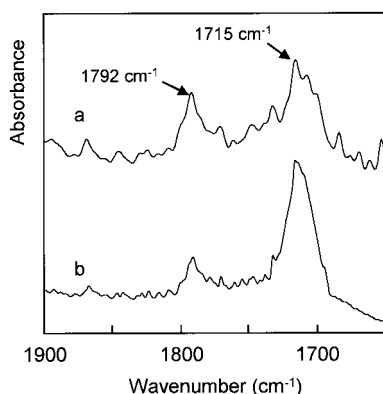
### Synthesis of a *Chlorella*-PE composite

*Chlorella* used in this study forms spherical and hollow aggregates of cells (3–5 μm in diameter) with an average diameter of 50 μm and a wall thickness ranging from 5 to 20 μm. It is noted that the cell wall primarily consists of α-cellulose (15%) and hemicellulose (31%),<sup>6</sup> both of which have OH groups available to react with MA for the formation of ester bonds.

Synthesis of a *Chlorella*-PE composite was tentatively explored by Procedure 1 to estimate the effects of MPE on the compounding, by examining the tensile properties of the products. Figure 1 shows the tensile strengths of the composites prepared under constant weight ratios of MPE to *Chlorella* (MPE/Ch) ranging up to 3/4. The tensile strength of the resultant composite strikingly increases with the ratio of MPE/Ch, attaining a maximum when the MPE/Ch ratio is greater than 2/4. This means that a lower-limited amount of MA groups on PE is satisfactory for effective



**Figure 2** Synthesis of *Chlorella*-PE composite through solid-phase reactions.

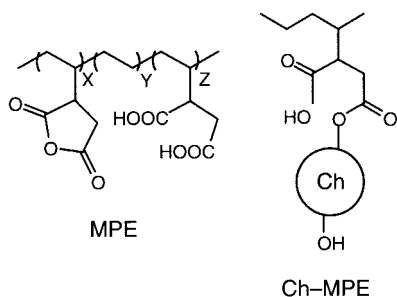


**Figure 3** FTIR spectra of (a) MPE prepared by Procedure 2 and (b) a reference MPE sample from Aldrich (MA content: 0.85 wt %).

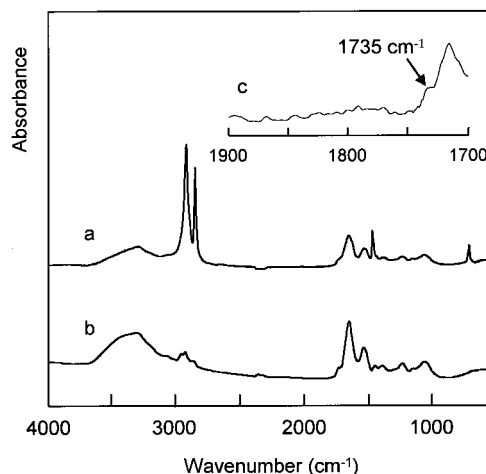
tive compounding of *Chlorella* with PE. Taking further account of the dispersion of MA groups in a PE matrix, we determined the amount of MA used in Procedure 2 composed of continuous processes (Fig. 2) to be 1/20 of that in Procedure 1, to develop a *Chlorella*-PE compound.

Successful formation of a *Chlorella*-MPE composite (Ch-MPE) through solid-phase reactions was confirmed by IR spectroscopy. IR spectra of MPE have two characteristic bands attributed to grafted succinic anhydride groups and their hydrolysis derivatives at 1792 and 1715  $\text{cm}^{-1}$  in Figure 3(a), respectively, with no bands attributed to poly(maleic anhydride) (1784  $\text{cm}^{-1}$ ) and free MA (1780  $\text{cm}^{-1}$ ).<sup>7</sup> Based on IR spectra of a reference of MPE purchased from Aldrich [Fig. 3(b)], we estimated that MPE obtained by Procedure 2 contains about 0.23 wt % MA, in agreement with 92% of added MA being grafted onto PE (Fig. 4).

The IR spectra of *Chlorella* are characterized by an absorption band attributed to OH groups at 3440  $\text{cm}^{-1}$ , accompanied by those attributed to second amide groups at 3312, 1654, and 1543  $\text{cm}^{-1}$  in Figure 5(b). The IR spectra of Ch-MPE are characterized by a lower intensity of absorption at 3440  $\text{cm}^{-1}$  than that of original *Chlorella*, the disappearance of the band at



**Figure 4** Chemical formulas of MPE and Ch-MPE.



**Figure 5** FTIR spectra of (b) *Chlorella* and (a) *Chlorella* (30 wt %)-MPE composite. The top right spectrum is a subtraction spectrum between the *Chlorella*-MPE composite (a) and *Chlorella* (b).

1792  $\text{cm}^{-1}$ , and the appearance of the new band attributed to ester groups at 1735  $\text{cm}^{-1}$  in Figure 5(a) and (c). This result strongly suggests that grafted MA groups on PE bond to OH groups of *Chlorella* by esterification (Fig. 4).

Synthesis of a *Chlorella*-PE composite by the procedure shown in Figure 2 has some significant advantages from a practical viewpoint. MPE with high reactivity can be obtained by solid-phase reactions, and *Chlorella* is successively compounded with MPE through the formation of ester bonds in a solid phase. Thus, it is noteworthy that the method consists of continuous and simple processes, and also yields no wastes, showing a significant contrast to those with solution phases.

#### Tensile properties of a *chlorella*-PE composite

Tensile properties of Ch-MPE were compared with those of a *Chlorella*-unmodified PE (UPE) composite (Ch-UPE) in the *Chlorella* content ranging up to 40 wt % (Fig. 6). From Figure 6, Ch-MPE exhibits a marked increase in tensile strength and Young's modulus, and thus a significant decrease in elongation. Furthermore, these behaviors are more significant with an increase in *Chlorella* content. The results are strongly consistent with the formation of chemical bonds between *Chlorella* and MPE.

SEM micrographs of a Ch-MPE fracture in Figure 7(a-1) and (a-2) reveal that *Chlorella* grains in Ch-MPE are firmly inlaid in the MPE matrix, without air gaps intervening between the *Chlorella* grains and the MPE matrix. Interestingly, when Ch-MPE is strained to failure, the *Chlorella* grains on the fracture are broken [Fig. 7(a-2)], suggesting that interactions between

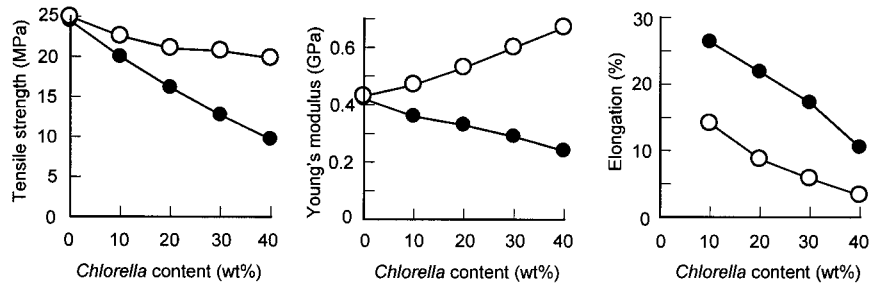


Figure 6 Tensile properties of Ch-MPE (○) and Ch-UPE (●).

*Chlorella* and MPE are stronger than those between *Chlorella* cells. These are completely different from the results for Ch-UPE in Figure 7(b), which proves no adhesion of *Chlorella* grains holding original shapes to the UPE matrix, leaving air gaps in the interfaces.

On the basis of the SEM observations, we can understand the tensile properties of a *Chlorella*-PE composite. The tensile strength of Ch-UPE ( $\sigma_{CUPE}$ ) is principally attributed to the contribution from the UPE matrix, and accordingly can be expressed as

$$\sigma_{CUPE} = \sigma_{UPE} \times A_{UPE}/A \tag{1}$$

where  $\sigma_{UPE}$  is the tensile strength of UPE,  $A_{UPE}$  is the sectional area of the UPE matrix, and  $A$  is the total cross-sectional area. On the other hand, the tensile strength of Ch-MPE ( $\sigma_{CMPE}$ ) is determined not only by the strength of the MPE matrix ( $\sigma_{MPE}$ ) but also by the strength of the *Chlorella* grains ( $\sigma_{Ch}$ ), and can be expressed by the following equation:

$$\sigma_{CMPE} = \sigma_{MPE} \times A_{MPE}/A + \sigma_{Ch} \times A_{Ch}/A \tag{2}$$

where  $A_{Ch}$  is the sectional area of the *Chlorella* grains. Because  $\sigma_{MPE} = \sigma_{UPE}$ , as clearly shown in Figure 6, eq. (2) may be rewritten into the following equation:

$$\sigma_{CMPE} = \sigma_{CUPE} + \sigma_{Ch} \times A_{Ch}/A \tag{3}$$

This equation proves that the tensile strength of Ch-MPE is greater than that of Ch-UPE by  $\sigma_{Ch} \times A_{Ch}/A$  and that the difference increases with an increase in *Chlorella* content. Thus, the tensile strength of Ch-MPE attains 19.93 MPa even at a *Chlorella* content of 40 wt %, more than 2 times greater than that of Ch-UPE (from Fig. 6).

**Moldings**

Ch-MPE can be readily shaped into a plate [size: 15 cm × 15 cm × 3–5 mm (width × length × thickness)]

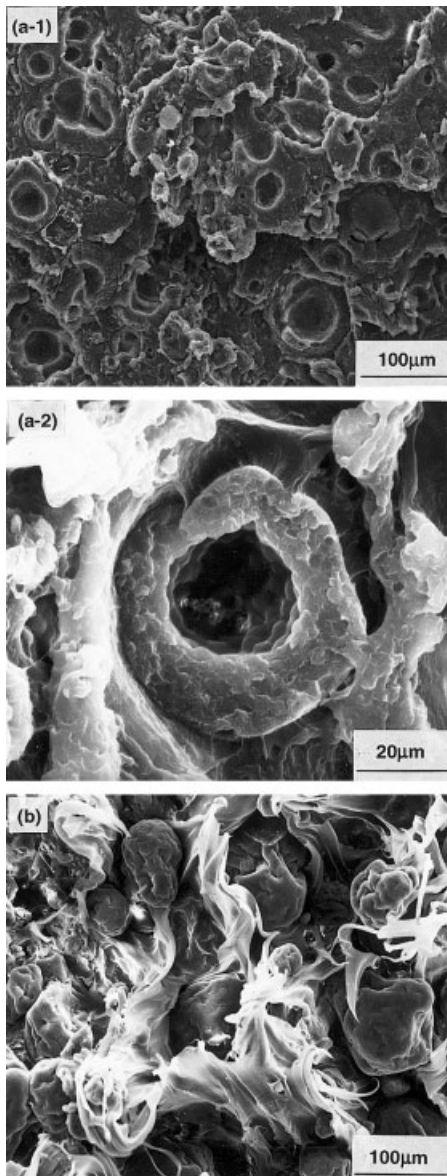
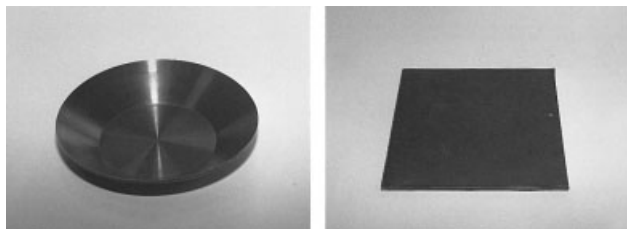


Figure 7 SEM micrographs of fractures of *Chlorella* (30 wt %)-MPE [(a-1) 100 μm; (a-2) 20 μm] and *Chlorella* (30 wt %)-UPE composites (b).





**Figure 8** Moldings of a *Chlorella*-PE composite with a *Chlorella* content of 30 wt %.

and a dish-type molding [size: 10 cm × 6 cm × 1.5 cm (upper diameter × bottom diameter × height)] by a heat-pressurizing method because of its thermal plasticity. Examples are given in Figure 8.

### CONCLUSIONS

We developed a novel composite of *Chlorella* and PE with satisfactory tensile properties through solid-phase reactions.

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