Strength Expression of *Chlorella*-Plastic Composite and its LCA

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The purpose is to elucidate strength expression mechanism of *Chlorella*-polyvinyl chloride (PVC) composite, and *Chlorella*-high density polyethylene (HDPE) composite. In the former, the tensile strength decreased as the *Chlorella* content increased, and the experimental results matched well the theoretical curve up to 20 wt.% of *Chlorella* content. The latter showed lower strength than the former because hydrophobic HDPE molecule could not react sufficiently with hydrophilic *Chlorella* grains. The tensile strength of *Chlorella*-HDPE composite was improved significantly by chemical modification of HDPE surface from hydrophobic to hydrophilic with maleic anhydride (MA) and benzoyl peroxide (BPO). The Life Cycle Assessment (LCA) for the *Chlorella*-PVC composite showed that 1.85×10^4 t-C/y could be cut down when *Chlorella* was used as substitute of plasticizer, di-2-ethylhexyl phthalate (DEHP), at the *Chlorella* production rate 1.74×10^4 t-dried algae/y from a photo-biological CO_2 fixation system with site area of about 2 km^2. We succeeded in making practicable sample of floor tile using *Chlorella*-PVC composite and *Chlorella*-HDPE composite, which could be ecofriendly building materials.

Keywords : *Chlorella* sp., PVC, Polyethylene, Composite, LCA

1. INTRODUCTION

Reduction of CO_2 emission into the atmosphere is very important issue for the sustainable development, because the increase of CO_2 in the atmosphere cause global warming. Research Institute of Innovative Technology for the Earth (RITE) has been conducted a research project of biological CO_2 fixation and utilization supported by New Energy and Industrial Technology Development Organization (NEDO) with participation of private companies for ten years from 1,990.

The concentration of CO_2 in the exhaust gas of Liquefied Natural Gas (LNG) power station is about 10 % in volume. The green micro-algae of the project, *Chlorella* UK-001, can grow well under the high concentration CO_2 and shows the CO_2 fixing ability, 50 g-$CO_2/m^2 \cdot d$ (weight per unit site area each day), which is ten times of moderate forest one.

A large amount of micro-algae produced in the system should not make CO_2 appear again into the atmosphere by its utilization. As a member of the project Ishikawajima-Harima Heavy Industries Co., Ltd. (IHI) has been carried out the research and development for utilization of *Chlorella* for building materials with

Shikoku National Industrial Research Institute (SNIRI), and has made *Chlorella*-polyvinyl chloride (PVC) composite [1], [2] and *Chlorella*-high density polyethylene (HDPE) composite [3].

In this work we describe the characteristics and the strength expression mechanism of these composites, and discuss the possibility of application for the building floor tiles. Furthermore we estimate the CO_2 reduction effect when the *Chlorella* is used partly for substitute of plasticizer, di-2-ethylhexyl phthalate (DEHP).

2. EXPERIMENTAL

2.1 Materials

Dried *Chlorella* powder (Yaeyama Ltd.) as the alternative of real photobioreactor products, PVC powder (n = 1100, Wako Pure Chemical Ind., Ltd.), and HDPE pellet (7,000F, MW $\fallingdotseq$ 2 $\times$ 10^5, Mitsui Chemicals, Inc.) were used in this work. The grain of *Chlorella* which was constituted of cells (about 5×10^{-6} m in diameter) was a nearly spherical aggregate (about 5 $\times 10^{-5}$ m in average size). HDPE was used as powder with a size of about 1 mm after mechanical pulverization.

2.2 Molding methods

Both of the composites were prepared by a heat pressurizing method. A aluminum mold frame with inner size of 120×20×7 mm was used for making samples. Thermocompressor (NSF-37, Shinto Metal Industries Ltd.) for molding was used with oil pressure apparatus and heating device.

2.3 Chemical modification of HDPE and preparation of composite

Chemical modification of HDPE and preparation of the composite were performed as follows [4]: Maleic anhydride (MA) and benzoyl peroxide (BPO) as the initiator were dissolved in acetone, and the acetone solution was then sprayed onto the HDPE powder until the weight ratio of MA : BPO : HDPE = 0.25 : 0.02 : 100. The mixture was well blended and treated at 160 °C for 30 min to modify the HDPE.

The modified HDPE (MPE) and *Chlorella* composite was prepared by feeding *Chlorella* into the MPE, mixing at 160 °C for 10 min , and finally shaping it into small pellets. Unmodified HDPE (UPE) and *Chlorella* composite was directly prepared by feeding the both powder into the mixer and mixed at 160 °C for 10 min.

Test sample sheets of the composite were prepared by heat pressurizing at 160 °C, 2.2 MPa, for 2 min.

2.4 Measurement

The test piece (sheet sample) was conditioned at 20 °C and 65 vol.% relative humidity in the room for 24 hour before measuring tensile strength and elongation. Test piece for the measurement was made according to the standard method [5]. The tensile tester (AG-100A, Shimadzu Ltd.) was used to measure tensile strength and elongation at break in accordance with testing method for tensile properties of plastics (cross-head speed of 5 mm/min.). Microstructure of the materials was observed by a Scanning Electron Microscope (S-2460N, Hitachi Ltd.).

Functional groups of *Chlorella* were determined by FTIR spectroscopy with a Spectrum 2000 spectrometer (Perkin-Elmer Ltd.).

3 . RESULTS AND DISCUSSION

3.1 Strength expression of *Chlorella*-PVC composite

The cell wall of *Chlorella* is principally made of cellulose, hemicellulose, fatty acid, and protein. There are hydrophilic group (hydroxyl, carboxyl etc.) on the cell surface. PVC is also hydrophilic polymer. It is assumed that the total section area of the composite (A)

equals the summation of the section area of PVC matrix (A_p) and the *Chlorella* part (A_c). The strength of the composite (ó) can be give by Equation (1).

$$ó = F / A \qquad (1)$$

where F is the tension load added on the composite. If the tensile strength of the composite is contributed only by the PVC matrix, the tension load can be calculated by Equation (2).

$$F = ó_p A_p \qquad (2)$$

where $ó_p$ is the tensile strength of PVC matrix. Introducing Equation (2) into Equation (1) yields Equation (3).

$$ó = ó_p A_p / A \qquad (3)$$

If there are no void (gas holes) in the composite, the volume of the composite (V) is the summation of the volume of PVC matrix (V_p) and *Chlorella* (V_c). V_p and V_c can be defined as

$$V_p = W_p / D_p \qquad (4)$$

$$V_c = W_c / D_c \qquad (5)$$

where W_p and D_p are the weight and density of PVC, and W_c and D_c are the weight and density of *Chlorella*, respectively. If all the cross sections of the composite have the same values of A_p and A_c, the following relation is considered.

$$A_p / A = V_p / V \qquad (6)$$

By using $V = V_p + V_c$, Equation(4), and Equation(5), Equation(6) can be rewritten as

$$A_p / A = 1 / (1 + D_p W_c / W_p D_c) \qquad (7)$$

The experimental values of D_c, D_p are 0.7 and 1.4, respectively. If the weight content of *Chlorella* in the composite is expressed as C %, W_c / W_p equals (C / 100) / (1 - C / 100), then by introducing Equation (7) into Equation (3), Equation (8) is obtained.

$$ó = ó_p [1 / \{1 + 2(C / 100) / (1 - C / 100)\}] \qquad (8)$$

The theoretical tensile strength values of the composite can be calculated by Equation (8). Figure 1 is the theoretical curve according to Equation (8) and the
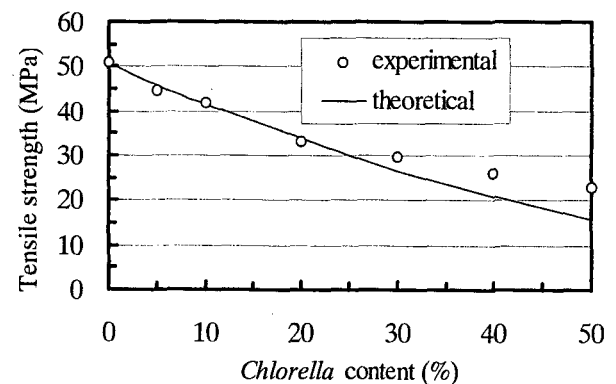

Figure 1. Relation between *Chlorella* content and tensile strength, *Chlorella*-PVC composite
Pressure:4.4MPa, Temp:180°C, Time: 5min.
Additives:KM-55, 0.5% in PVC

experimental values. The experimental values match up to the theoretical curve when the content of *Chlorella* is lower than 20 wt.%, and the difference gradually increases with *Chlorella* content increased. It can be considered that the strength of the composite is mainly from PVC matrix when the *Chlorella* content is lower than 20 wt.%, and the interface combination of *Chlorella* and PVC plays an increasing role in the strength of the composite. The tensile strength of the composite at 20 wt.% of *Chlorella* content is over 30 MPa, and can meet the standard [6].

3.2 Strength expression of *Chlorella*-HDPE composite

Benzoyl peroxide (BPO) initiates radical formation on the HDPE backbone by H abstraction. The radicals then react with maleic anhydride (MA) to form modified HDPE (MPE). The tensile strength of *Chlorella*-UPE composite decreased with *Chlorella* content increased, and the curve crossed the line of the standard value (15 MPa) [7] at 20 wt.% of *Chlorella* as shown in Figure 2. For comparison the tensile strength of *Chlorella*-PVC composite, which is larger than that of *Chlorella*-UPE curve was shown in Figure 2, and also the strength value of *Chlorella*-MPE effect in Figure 2.
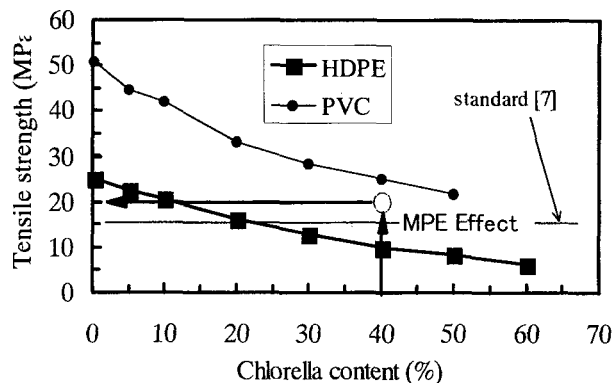
Figure 2. Effect of *Chlorella* content in the mixture on tensile strength

    HDPE   Pressure:2.2MPa, Temp:160℃, Time:2min.
    PVC   Pressure:4.4MPa, Temp:180℃, Time:5min.

An IR spectrum of *Chlorella* is shown in Figure 3a. The absorption band at 3,440 cm^{-1} is assigned to OH groups, it suggests that *Chlorella* contains cellulose and hemicellulose. From Figure 3c a lower intensity of absorption at 3,440 cm^{-1} was observed compared with *Chlorella* itself, on the other hand the band at 3,440 cm^{-1} of the *Chlorella*-UPE composite still remained in shown Figure 3b. The difference spectrum between the spectra of the *Chlorella*-MPE composite and *Chlorella* indicate the appearance of the new band at 1,735 cm^{-1} caused by
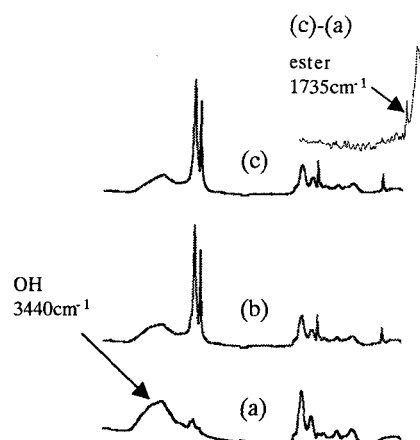
Figure 3.   IR spectra of *Chlorella* (a), *Chlorella*-UPE (b), and *Chlorella*-MPE (c)

ester group as shown in the top-right part of Figure 3. It suggest that a chemical bond by esterification took place between MA groups of MPE and OH groups of *Chlorella*.

The tensile strength of *Chlorella*-MPE composite is 20 MPa, which is twice as large as the *Chlorella*-UPE at the 40 wt.% of *Chlorella* content.

3.3 Substitution effect of *Chlorella* for conventional plasticizer of PVC floor tiles

Assumption : A photobioreactor system fixing CO_2 emitted from the 1,000 MW LNG power station is investigated from the point of view of Life Cycle Assessment (LCA). The micro-algae, *Chlorella*, discharged from the system can be applicable to the building floor tiles. The CO_2 fixation rate of the system is assumed 50 g-CO_2/ m^2·d as mentioned above, and the annual fixation amount is 1.28×10^4 t-CO_2/km^2·y at the operation rate of 70 %. The slurry of the micro-algae is dehydrated from 80 wt.% to 10 wt.% by using a excess energy of the power station. After drying of the wet algae, the product is used for the substitute of the plasticizer.

Drying power consumption : The thermal energy required for drying of wet algae (temperature 30 ℃) to make dried algae is 2.84×10^3 kcal/kg-dried algae, in which the drying temperature is 100 ℃, and the thermal loss is assumed 25 %. The 1 kg of dried micro-algae is produced from the 4.50 kg of wet micro-algae, therefore the electric power requirement is 1.26 kWh/kg-dried algae as 1 kWh equals to 2.25×10^3 kcal.

CO_2 balance of system : The amount of CO_2 emission to make 1 kg of the substitute (dried micro-algae) is 1.43×10^{-1} kg-C/kg-dried algae by using the

electric power requirement, 1.26 kWh/kg-dried algae, and the basic CO_2 unit as carbon, 1.135×10^{-1} kg-C/kWh (a Japanese statistical data). As the amount of wet micro-algae is 4.50 kg per 1kg of dried micro-algae, the fixation amount of CO_2 into the micro-algae is 3.53×10^{-1}kg-CO_2/kg-wet algae or 1.59 kg-CO_2/kg-dried algae. Finally the CO_2 emission-fixation balance is expressed as fixation of 2.91×10^{-1} kg-C/kg-dried algae.

CO_2 emission from the conventional plasticizer production : The main substances are phthalic anhydride, and 2-ethylhexanol to make the conventional plasticizer, di-2-ethylhexyl phthalate (DEHP). PVC floor tiles are consisting of rigid compound and plasticized compound, and the content of the plasticizer is less than 10 wt.% in the former, 25~50 wt.% in the latter. It is assumed that the production of the floor tiles is 9.64×10^4 t/y (The Encyclopedia of Practical Plastics, Sangyo Tyosakai, 1994), and the content of plasticizer and PVC is 28 wt.% and 72 wt.% respectively, further the 28 wt.% of plasticizer is broken down into 18 wt.% of the micro-algae as the substitute and 10 wt.% of the plasticizer as the rest. The amount of the each materials is calculated as 9.64×10^3 t/y of the plasticizer (10 wt.%), 1.74×10^4 t-/y of the micro-algae (18 wt.%), and 6.94×10^4 t/y of the PVC (72 wt.%) respectively. As the amount of CO_2 emission is 7.71×10^{-1} kg-C per 1 kg of the conventional plasticizer by the another estimation, the effect of the substitution on CO_2 reduction is calculated as 1.34×10^4 t-C/y.

Total CO_2 reduction effect : Finally the total amount of CO_2 reduction is 1.85×10^4 t-C/y (6.79×10^5 t-CO_2/y), the summation of CO_2 reduction by the micro-algae is 5.06×10^3 t-C/y, and the substitution effect by the micro-algae is 1.34×10^4 t-C/y, in which the production of micro-algae as the substitute is 1.74×10^4 t-dried algae/y.

Energy saving effect : The effect of energy saving on the substitution is estimated as 1.57×10^4 t-oil/y by using the amount of energy consumption, 9.93×10^3 kcal per 1 kg of the conventional plasticizer by the another data, and the oil energy, 1.10×10^4 kcal/kg-oil, at the production of 1.74×10^4 t-dried algae/y.

Site area required for the system : The CO_2 fixation amount of the system is 2.77×10^4 t-CO_2/y derived from the production of the dried micro-algae, and the carbon content (48.2 wt.%). As the amount of emission of 1,000 MW LNG power station is 1.74×10^6 t-CO_2/y, it is estimated the CO_2 reduction rate is 1.5 wt.%, and corresponds to 2.2 km² of the site area for the system by using the assumption, 1.28×10^4 t-CO_2/ km²·y (fixation rate 50 g-CO_2/ m²·d, the operation rate 70 %).

4. CONCLUSION

The mechanisms of strength expression for the *Chlorella*-PVC composite and the *Chlorella*-HDPE composite was elucidated. It is important how the chemical interaction between *Chlorella* and the plastics (PVC, HDPE) can be produced to make more strong composite. In particular it is very effective to modify HDPE from hydrophobic to hydrophilic with some chemicals. In the case of the *Chlorella*-MPE composite it is possible to contain a large amount of *Chlorella* into the composite, which is practical to find a market for the mass-produced floor tiles.

LCA suggest that *Chlorella* as a part of substitute of the PVC plasticizer can contribute for reducing CO_2 emission at the conventional mass production of PVC floor tiles in the industries.

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