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Synthesis and characterization of a novel blend of polypropylene with *Chlorella*

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A novel blend of polypropylene (PP) with *Chlorella*, a natural microalga, was synthesized successfully by a melt-mixing method with maleic anhydride-modified polypropylene (MPP) as a compatibilizer. The adhesion of hydrophobic PP to hydrophilic *Chlorella* is based on the formation of chemical bonds between the maleic anhydride groups of MPP and hydroxy groups of *Chlorella* through solid-phase esterification. The single maleic anhydride groups have the highest reactivity with *Chlorella*. From the comparison with PP–*Chlorella* blends without MPP, the ester bonds between MPP and *Chlorella* cause a decrease in crystallinity of the MPP matrix which is a primary origin of the decrease in melting and solidification enthalpies of the MPP–*Chlorella* blend, and induce intensive expansion of the MPP matrix around the *Chlorella* particles which decreases the glass transition temperature. Consequently, the PP–*Chlorella* blend with MPP exhibits a marked increase in tensile strength and Young's modulus compared with the blend without MPP because of the stronger interactions between MPP and *Chlorella* than those between *Chlorella* cells.

Introduction

We have directed much attention to *Chlorella*, a kind of microalga belonging to the Chlorophyceae, from the viewpoint of photosynthetic fixation of CO_2 for the prevention of global warming, because of its high utilization rate (10–20%) of light energy compared with common plants (0.1–0.5%).[1,2] A fixing rate of CO_2 greater than $1\ \mathrm{kg}\ \mathrm{CO_2}\ \mathrm{m^{-3}}\ \mathrm{day^{-1}}$ has been achieved by *Chlorella* with solar light.[3] How to make effective use of the microalga following biological fixation of CO_2 is an important problem. Thus, we have conducted various studies to explore the utilization of the microalga. One of these studies involves using the microalga as a filler in thermoplastics, aiming at developing building or other functional materials.

Very little has been reported on the potential application of algae in polymer compounds. *Cladophora glomerata*, an alga with a filamentous structure, is the only example that has been reported as a filler in polystyrene resin, destructurized starch and polycaprolactones,[4] but no evidence has been presented of the interaction between the alga and matrix components. In a previous study,[5] we reported briefly on the synthesis of a novel composite of polyethylene with *Chlorella* by a melt-mixing method. A composite of hydrophobic polyethylene with hydrophilic *Chlorella* has been achieved through solid-phase reactions characterized by pre-modification of polyethylene with a small amount of maleic anhydride. We demonstrated the formation of ester bonds between maleic anhydride groups grafted on to the polyethylene and hydroxy groups on the cell walls of *Chlorella*.

Design and elucidation of the interaction between *Chlorella* and hydrophobic plastics is essential for the development of novel composites with good mechanical properties. Polypropylene can also be modified by grafting maleic anhydride monomers on to the polymer, but it is expected that the grafting groups on polypropylene are different from those on polyethylene, particularly in the location and structure of the grafting which affects the compatibility with *Chlorella* and accordingly the properties of the blend. Furthermore, because of the semicrystallinity of polypropylene, the change in crystallinity on blending with *Chlorella* is very interesting for understanding the interaction between the matrix and *Chlorella*. In this study, we synthesized a novel blend of polypropylene and *Chlorella* with polypropylene-*graft*-maleic anhydride (MPP) as a compatibilizer by a melt-mixing method, and describe the interaction mode of *Chlorella* and MPP. On the basis of structural features of the interfaces between *Chlorella* and the polypropylene matrix, we discuss the tensile properties of the resultant polypropylene–*Chlorella* blend.

Experimental

Materials

Chlorella used in this study was supplied by Yaeyama Shokusan Inc. (Japan). The original *Chlorella* (OCH) forms aggregate grains with an average grain size of about 50 μm (Fig. 1a). The aggregate grains consist of *Chlorella* cells with diameters of about 3–5 μm, forming hollow spheres with walls about 5–20 μm thick.[5] OCH was ground to yield a sample of ground *Chlorella* (GCH) with an average particle size of about 4 μm, fragments of the grain walls (Fig. 1b). Isotactic polypropylene (iPP) with an average molecular weight of *ca.* 250 000 and a density of $0.9\ \mathrm{g\ cm^{-3}}$, and polypropylene-*graft*-maleic anhydride (MPP) containing 0.6 wt% maleic anhydride were purchased from Aldrich Chemical Co., Inc.

Blends and their preparation

Compatibilized polypropylene–*Chlorella* blends (CPP–OCH) with MPP as a compatibilizer were synthesized fixing the weight ratio of MPP/*Chlorella* = 0.5, in contrast to uncompatibilized polypropylene–*Chlorella* blends (UPP–OCH) without MPP. For blend characterization, ground *Chlorella* (GCH) was blended with UPP, CPP, and MPP. All of the blends were synthesized using a roller mixer with a chamber volume of $60\ \mathrm{cm^3}$ (R60 type, Toyo Seiki Seisakusho, Japan) according to the previous study.[5] The different mixtures of PP, MPP, and *Chlorella* were melt-mixed at 80 rpm and 180 °C for 20 min,

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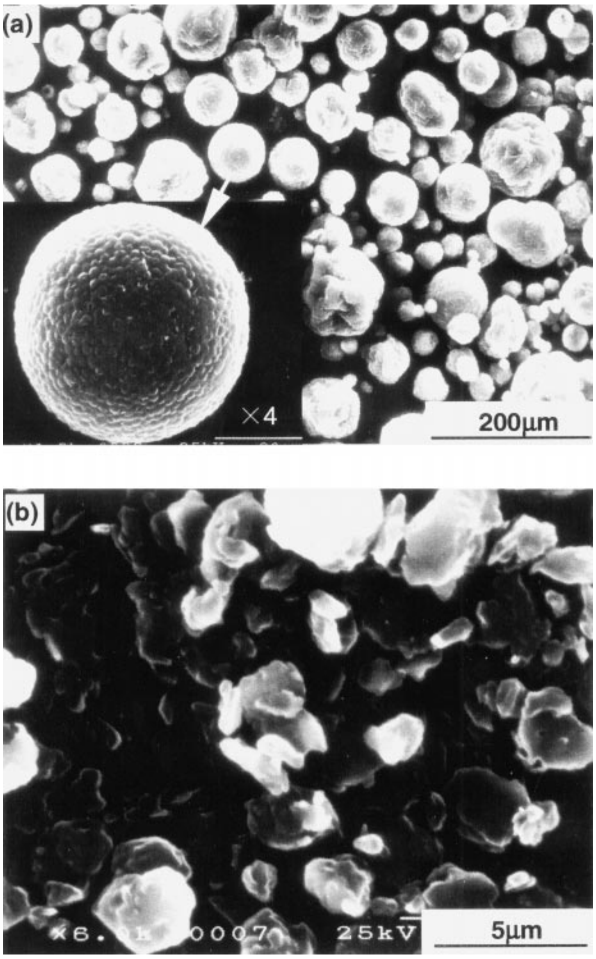


Fig. 1 Original *Chlorella* aggregates consisting of *Chlorella* cells (a) and ground *Chlorella* (b).

and then were hot-pressurized (180 °C, 3 MPa, 2 min) into the sample sheet for the standard tensile test.[6] For preparing test samples for DMA measurement, blends were placed between sheets of aluminium foil in a press maintained at 180 °C and 0.5 MPa for 2 min, and then were slowly cooled to room temperature at a rate of 5 °C min^{-1}.

Analysis methods

Tensile tests. The sample sheets were conditioned at 20 °C and 65% relative humidity in an environmental chamber for 24 h before the tensile test with a tensile tester (AG-100A, Shimadzu, Japan) at a strain speed of 20 mm min^{-1} according to the testing method for tensile properties of plastics.[6]

SEM observation of fractures. To minimize the deformation of their fractures, the rectangular blend samples were immersed in liquid nitrogen for 10 min, before obtaining fractures. The fractures were then coated with a thin gold–palladium layer prior to observation with a Hitachi model S-2460N model scanning electron microscope (SEM) at 25.0 kV.

FT-IR. Blends were crushed together with KBr using a JFC-300 model cryogenic sample crusher (Nippon Bunseiki Co., Ltd.) with liquid nitrogen as a coolant. FT-IR spectra of KBr-pellet samples were recorded on a spectrum 2000 spectrometer (Perkin-Elmer Co., Ltd.) with a resolution of 2 cm^{-1} in the spectral range of 4000–370 cm^{-1}.

DSC and DMA analyses. Melting and solidification temperatures and enthalpies of the blends were determined with a Perkin-Elmer Pyris 1 DSC apparatus at a heating and a cooling rate of 5 °C min^{-1}. The heating–cooling cycles for each sample were repeated twice, and the result from the second cycle was adopted because the differential scanning calorimetry (DSC) curves after more than two cycles were consistent with each other. Dynamic thermal mechanical analysis (DMA) of the blends was performed with a Perkin-Elmer DMA 7e using a three point bending–rectangular measuring system. The size of the rectangular samples was 20 × 5 × 1 mm (length × width × height). Indium and ice were used for temperature calibration of the apparatus. The measurements were carried out under a 550 mN static force and a 500 mN dynamic force at 1 Hz frequency, and a heating rate of 5 °C min^{-1}.

Results and discussion

IR spectra

IR spectra of PP and MPP are shown in Fig. 2. The obvious difference between them appears in the range from 1900 to 1700 cm^{-1}. From the magnified spectra, MPP exhibits four observable absorption bands; three overlapping bands at 1792, 1782, and 1773 cm^{-1} and a single band at 1716 cm^{-1}. In this range, PP exhibits no absorption bands. It has been reported that maleic anhydride derivatives have strong symmetric C=O stretching bands at wavenumbers 1770–1800 cm^{-1} as well as weak asymmetric C=O stretching bands around 1850 cm^{-1},[7] which are not observed in Fig. 2b, probably due to the low concentration of maleic anhydride (0.6 wt%). Of the three overlapping bands, the band at 1792 cm^{-1} is due to single saturated anhydride groups, and the broader band at 1782 cm^{-1} is due to poly(maleic anhydride) groups grafted on PP,[7] since it still appears after excluding non-grafted poly(maleic anhydride) by washing crushed MPP powder with acetone under reflux. We examined the assignment of the band at 1773 cm^{-1}, based on IR spectra of a model compound, poly(ethylene-*alt*-maleic anhydride) from Aldrich (catalog

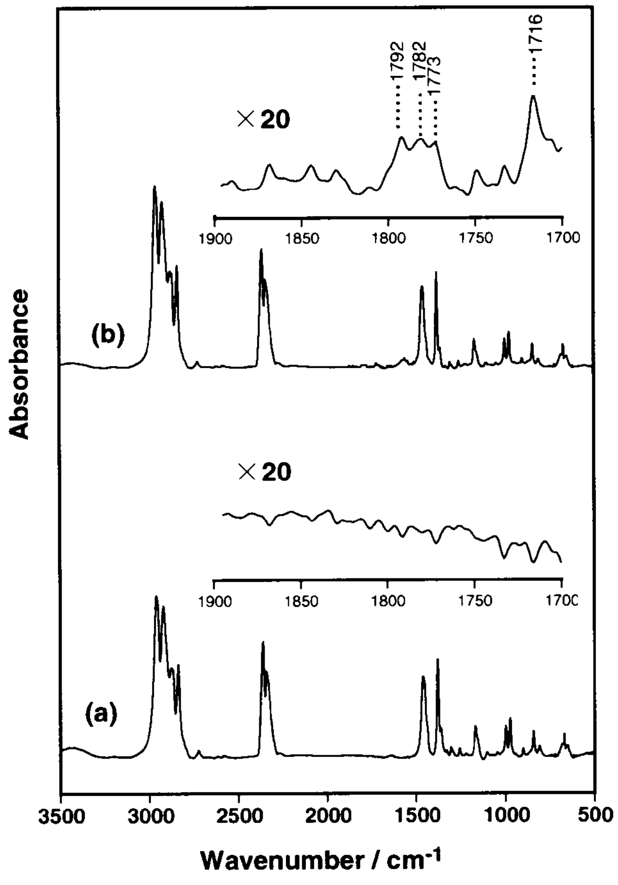
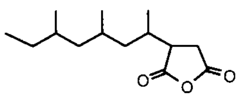
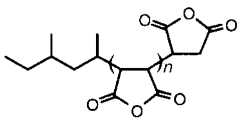
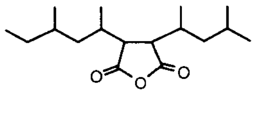
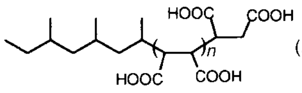


Fig. 2 FT-IR spectra of PP (a) and MPP (b).

number 18805-0).[8] This model compound exhibited two characteristic absorption bands at 1774 and 1855 cm^{-1}, due to symmetric and asymmetric C=O stretching, respectively. Accordingly, the absorption band of MPP at 1773 cm^{-1} is probably due to maleic anhydride units inserted in mainchains of PP. Generally, end-chain grafting is considered to be dominant in the grafting of maleic anhydride on PP because of the β-scission of PP chains.[7,9–11] The band at 1716 cm^{-1} is due to hydrolysis products of maleic anhydride groups.[7,12] Thus, the assignments of characteristic IR bands of MPP is given in Table 1.

An IR spectrum of *Chlorella* is shown in Fig. 3a. The absorption band at 3439 cm^{-1} is assigned to OH groups, while the absorption bands at 3312, 1654 and 1543 cm^{-1} are due to second amide groups. The existence of hydroxy groups strongly suggests that *Chlorella* contains cellulose and hemicellulose. Compared with *Chlorella* in Fig. 3a, a MPP–*Chlorella* blend containing 80 wt% MPP and 20 wt% GCH (referred as 80MPP–20GCH, hereafter) exhibits a lower intensity of absorption at 3440 cm^{-1} (Fig. 3c), well consistent with the case of a maleic anhydride modified polyethylene (MPE)–*Chlorella* composite;[5] in contrast, a UPP–*Chlorella* blend with 80 wt% PP and 20 wt% GCH (denoted as 80UPP–20GCH) causes hardly any change in absorption intensity at 3440 cm^{-1} compared with *Chlorella* (Fig. 3b). Furthermore, a difference spectrum between the MPP–GCH blend and *Chlorella* with respect to the band at 1543 cm^{-1} is shown in Fig. 3e. Different from the spectrum of MPP (Fig. 2b), the band at 1792 cm^{-1} disappears completely and the intensities of bands at 1782 and 1773 cm^{-1} decrease considerably, while a new band due to ester groups appears at 1732 cm^{-1}, suggesting an extensive esterification reaction between MPP and *Chlorella*.[5,13,14] The broader absorption band at 1732 cm^{-1} than that of the MPE–*Chlorella* composite in which MPE has predominantly single maleic anhydride groups,[5] indicates that the esterification reaction is more complicated in the MPP–*Chlorella* blend, because MPP has three classes of maleic anhydride groups involved in the esterification reaction. The difference in esterification among the three classes of maleic anhydride groups may be due to the steric hindrance which dominates their approach to hydroxy groups of *Chlorella*. Fig. 3e shows clearly that the single maleic anhydride group is the most reactive because of the complete disappearence of absorption at 1792 cm^{-1}.

Table 1 Assignment of IR bands of MPP

Bands/cm^{-1}	Functional groups
1792	
1782	 (*n* = 1,2,3...)
1773	
1716	 (*n* = 0,1,2...)

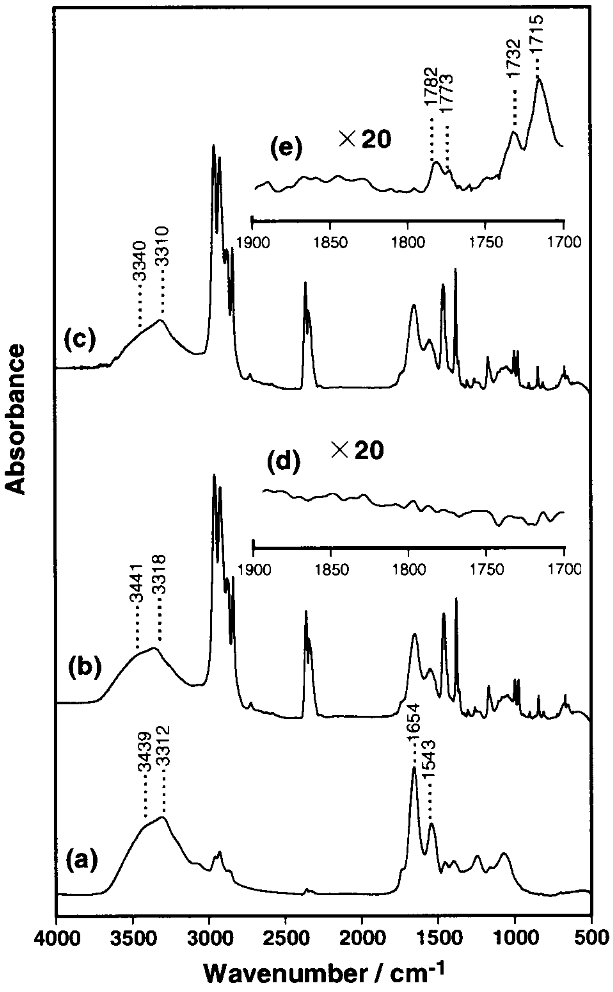


Fig. 3 FT-IR spectra of *Chlorella* (a), 80UPP–20GCH blend (b), and 80MPP–20GCH blend (c). The magnified spectra represent the difference spectra between 80UPP–20GCH blend and *Chlorella* (d), and between 80MPP–20GCH blend and *Chlorella* (e), respectively.

Crystallinity of blends

The effect of the chemical bonds between MPP and *Chlorella* on the crystallinity of the PP matrix is of great interest because polypropylene is a semicrystalline polymer. For a semicrystalline polymer, its crystallinity depends on the content of the ordered phase, which is defined as the molar fraction of chain atoms which possess a specified steric configuration related to their immediate neighbors along the chain. In an IR spectrum of PP, the absorption bands at 1168, 998, 899, and 842 cm^{-1} are due to the crystalline phase, while the absorption band at 974 cm^{-1} is due to the amorphous or irregular phase.[15,16] The crystallinity of PP can be estimated from the absorbance ratio of the band at 998 cm^{-1} to the band at 974 cm^{-1}, A_{998}/A_{974}, using eqn. (1):[15,17]

$$\text{Crystallinity(wt\%)} = 109 \times (A_{998} - A_{920})/(A_{974} - A_{920}) - 31.4 \quad (1)$$

where the absorbance at 920 cm^{-1}, A_{920}, is used for the background correction for best reproducibility.

To investigate changes in crystallinity of PP and MPP matrixes by their blending with GCH, the difference spectra between 80UPP–20GCH blend and GCH and between 80MPP–20GCH blend and GCH were compared with the spectra of PP and MPP in the range between 1200 and 800 cm^{-1}. Table 2 shows the absorbance ratios $(A_{998}-A_{920})/(A_{974}-A_{920})$ and the crystallinities of the two polymers and

Table 2 Crystallinity index of PP calculated from FT-IR results

	$(A_{998}-A_{920})/(A_{974}-A_{920})$	Crystallinity (wt%)
PP	0.805	56.3
80UPP–20GCH blend	0.798	55.6
MPP	0.792	54.9
80MPP–20GCH blend	0.732	48.8

their blends with *Chlorella*. By blending with GCH, the crystallinity of MPP decreases significantly, while that of PP remains almost unchanged. The marked decrease in crystallinity of MPP is probably due to the difficulty in steric ordering of MPP chains covalently bound to rigid *Chlorella*.

DSC characteristic of blends

DSC behaviours of 80UPP–20GCH and 80MPP–20GCH blends were characterized in comparison with those of PP and MPP. Because *Chlorella* does not undergo any significant change below 200 °C,[18] the melting and solidification phase transitions of the blend are entirely due to PP and MPP. The onset temperatures and enthalpies for melting and solidification phase transitions are summarized in Table 3. The 80UPP–20GCH blend exhibits melting and solidification enthalpies well consistent with 80% of those of neat PP at almost the same onset temperatures of the corresponding phase transitions, demonstrating similar DSC behaviours to those of PP. This indicates that the PP matrix in the 80UPP–20GCH blend is almost identical to neat PP, that is, PP has no interaction with GCH in the blend.

On the other hand, the 80MPP–20GCH blend has melting and solidification enthalpies smaller than 80% of those of neat MPP, exhibiting a broader DSC signal in melting with a little lower onset temperature (Table 3). The enthalpy of a phase transition for a semicrystalline polymer depends primarily on the crystallinity of the polymer.[19–22] Accordingly, the decrease in melting and solidification enthalpies of 80MPP–20GCH is probably due to the increase in content of the amorphous phase of MPP after the blending with *Chlorella* described in Table 2.

T_g of the blends

The glass transition temperature (T_g) of a blend is very important to understand the interaction modes between blend components. Since DSC measurements were not sensitive for observing T_g points of the blends, their T_g values were determined by dynamic mechanical analysis (DMA).[23] Fig. 4 shows DMA plots of PP, MPP, and their blends with *Chlorella*, where tan δ is defined as the ratio of loss modulus to storage modulus. The temperature at maximum tan δ corresponds to T_g. T_g of PP has been reported to range from −30 to +20 °C, depending on the tacticity and thermal history of the sample.[24] From Fig. 4, T_g of PP (about 1 °C) is almost the same as that of MPP. The T_g values of 80UPP–20GCH and 80MPP–20GCH blends decrease by about 3 °C and 8.5 °C from those of neat PP and MPP, respectively. In the PP–*Chlorella* blends, the T_g of *Chlorella* is expected to be much higher than neat PP and MPP, because *Chlorella* is a kind of rigid matter without viscoelasticity. However the addition of GCH causes a decrease in the T_g of PP in Fig. 4. This interesting result may be attributed to both the characteristics of *Chlorella* and the formation of chemical bonds between MPP and *Chlorella*. The T_g of a polymer is related to the movement of segments of polymer chains in free spaces.[25–28] *Chlorella* is a material consisting of diverse substances with different molecular weights. Although it does not experience any significant change below 200 °C, *Chlorella* still contains a small amount of substances with lower molecular weights which are volatile and decompose at the melt-blending temperature.[18] During melt-blending with PP and MPP, some volatile and/or decomposable substances may penetrate into the amorphous part of PP and MPP, causing swelling of some parts of the PP molecular chains. This may induce movement of the segments, leading to the depression in T_g of PP in the 80UPP–20GCH blend. On the other hand, for the 80MPP–20GCH blend with chemical bonds between MPP and GCH as described earlier, the formation of chemical bonds significantly restricts the stable arrangement of MPP chains bound onto GCH particles and results in their coarse entanglement with other MPP and PP chains. Thus the resultant volume expansion near the surfaces of the GCH particles will cause significant motion of the segments of MPP and PP chains there,[23] exhibiting a further decrease in T_g of the 80MPP–20GCH blend compared to the 80UPP–20GCH blend with no chemical bonds between UPP and *Chlorella*. Additionally, the greater tan δ of 80MPP–20GCH than of neat MPP is consistent with the crystallinity index of the former being lower than that of the latter (Table 2).

Table 3 Melting and solidification data of PP obtained from DSC analysis

Polymers and their blends	Melting Onset/ °C	Enthalpy /J g^{-1}	Solidification Onset/ °C	Enthalpy/ J g^{-1}
PP	155.8	90.5	120.7	−94.2
80UPP-20GCH	156.2	72.8	121.5	−76.5
MPP	155.1	93.8	126.9	−94.0
80MPP-20GCH	153.2	69.6	126.0	−70.9

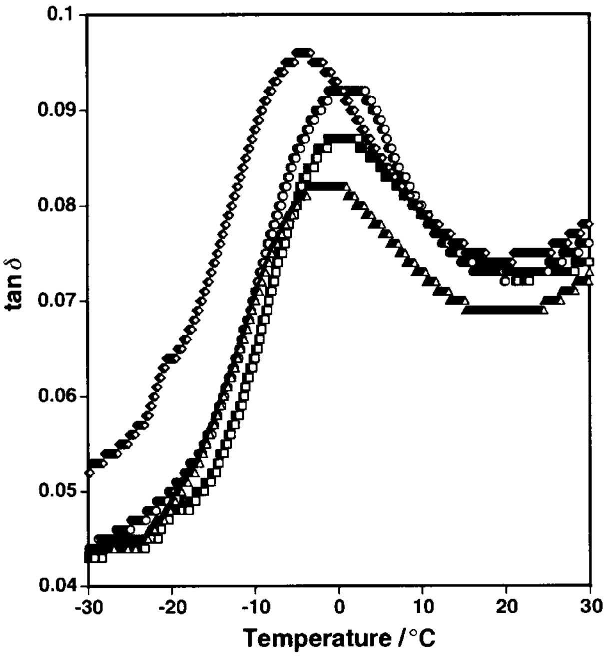


Fig. 4 DMA plots of PP (□), MPP (○), 80UPP–20GCH blend (△), and 80MPP–20GCH blend (◊).

Tensile properties of blends

Tensile properties of the CPP–OCH blends with different *Chlorella* contents are shown in Fig. 5, and are compared with those of the UPP–OCH blends in order to consider the effects of MPP in blending of PP with *Chlorella*. The tensile strength of the CPP–OCH blend decreases with an increase in *Chlorella* content, more gradually than that of the UPP–OCH blend without MPP. The difference in tensile strength between the CPP–OCH blend and the UPP–OCH blend becomes greater with an increase in *Chlorella* content. Accordingly, the CPP–OCH blend exhibits a tensile strength of 19.5 MPa at a *Chlorella* content of 50 wt%, more than 2 times as great as that of the UPP–OCH blend. It is very interesting that the Young's

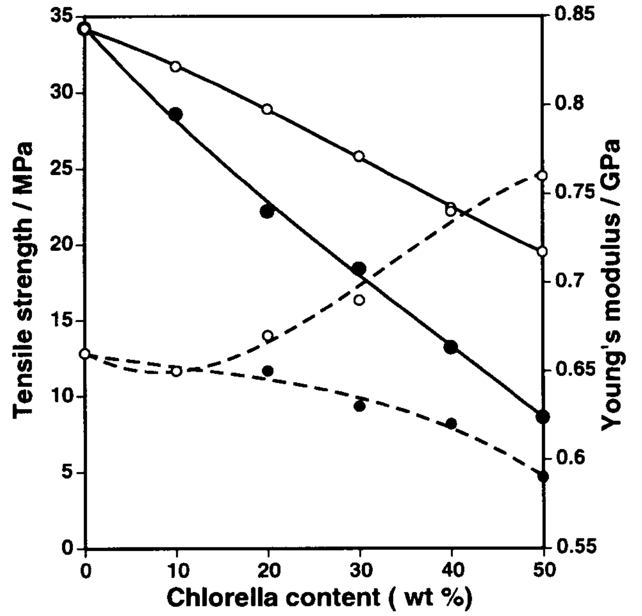


Fig. 5 Effects of OCH content on the tensile strength (——) and Young's modulus (------) of the UPP–OCH (●) and CPP–OCH blends (○).

modulus of the CPP–OCH blend increases with an increase in *Chlorella* content, while that of the UPP–OCH blend decreases. These results reflect very well the strong interactions between *Chlorella* and MPP, because the MPP matrix itself exhibits almost the same tensile strength and Young's modulus as the PP matrix. The interaction between *Chlorella* and MPP depends principally on chemical bonds between OH groups of *Chlorella* and maleic anhydride groups of MPP through esterification described earlier.

Fig. 6 shows the influence of morphology of *Chlorella* particles (GCH and OCH) on the tensile properties of the CPP blend. The CPP–GCH blend has higher tensile strength and elongation than the CPP–OCH blend does both at 10 wt% (Fig. 6a) and at 30 wt% *Chlorella* content (Fig. 6b). The 90CPP–10GCH blend has a tensile strength of 35.3 MPa, greater than that of neat bulk PP (34.2 MPa). When the content of *Chlorella* increases from 10 to 30 wt%, both blends break more easily maintaining a linear relationship between tensile strength and elongation to yield lower tensile strength and elongation. OCH is a spherical aggregate with a hollow structure consisting of single cells, while GCH is fragments of ground OCH (Fig. 1). Thus the results mentioned above indicate that the tensile properties of the blend depend significantly on the morphology of *Chlorella*, in terms of the efficiency in chemical bonding with MPP and in dispersion.

Fractures of the blends

Micrographs of fractures of three blends (70UPP–30OCH, 70CPP–30OCH, 70CPP–30GCH) are presented in Fig. 7. From Fig. 7, *Chlorella* grains in the 70CPP–30OCH (55PP–30OCH–15MPP) blend are well inlaid in the CPP matrix, with no air gaps between the *Chlorella* grains and the CPP matrix (Fig. 7b), in strong contrast to those in the 70UPP–30OCH blend which show no adhesion with the PP matrix leaving air gaps in the interface (Fig. 7a). Fig. 7b shows that the interaction between *Chlorella* grains and the CPP matrix in the 70CPP–30OCH blend ($\sigma_{\text{p–c}}$) is stronger than that between *Chlorella* cells ($\sigma_{\text{c–c}}$) which is primarily due to hydrogen bonds, because the *Chlorella* grains are split into two on fracture, and keep their original shape. This is well consistent with the formation of chemical bonds described earlier. These features of the fractures of PP–*Chlorella* blends are very similar to those of PE–*Chlorella* composites,[5] and suggest that the weight ratio of MPP/*Chlorella* = 0.5 is sufficient to form strong interactions between the CPP matrix and *Chlorella*. As GCH particles are well blended with the matrix, the interfaces between the GCH particles and the CPP matrix can hardly be distinguished (Fig. 7c), and there are no holes in the blend compared to the hollow holes of OCH in the CPP–OCH blend (Fig. 7b). The SEM observations clearly demonstrate that the microstructure in the interface between *Chlorella* and the PP matrix determines the tensile properties of the blend.

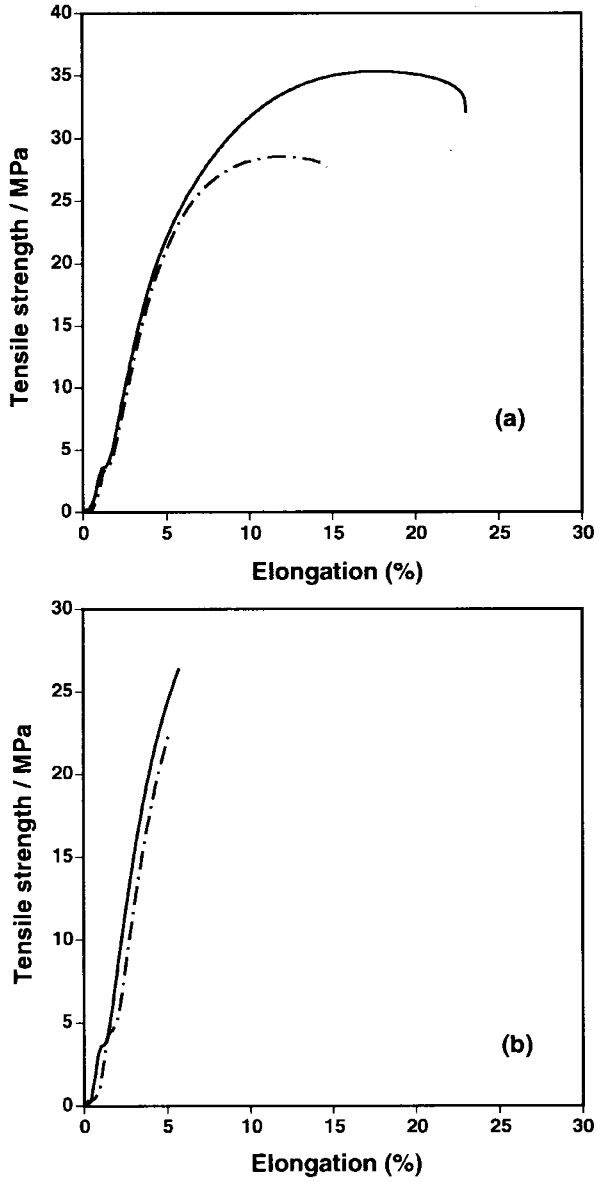


Fig. 6 Tensile properties of the CPP–GCH blend with the ground *Chlorella* (——), and the CPP–OCH blend with original *Chlorella* (–·–) at *Chlorella* contents of 10 wt% (a) and 30 wt% (b).

A structural model of the blend

On the basis of the above results, a structural model of the blend is proposed in Fig. 8, and is consistent with the thermal and mechanical behaviors of the blend. For a UPP–*Chlorella* blend, because no adhesion exists between *Chlorella* and the UPP matrix, *Chlorella* is completely separated from the UPP matrix with air gaps at the interface (Fig. 8a). For a CPP–*Chlorella* blend, on the other hand, *Chlorella* is in tight contact with the CPP matrix because of chemical bonds between *Chlorella* and MPP, with no air gaps at the interface. As the result of chemical bonds, the amorphous phase in the CPP matrix develops after blending with *Chlorella*, and expansion of

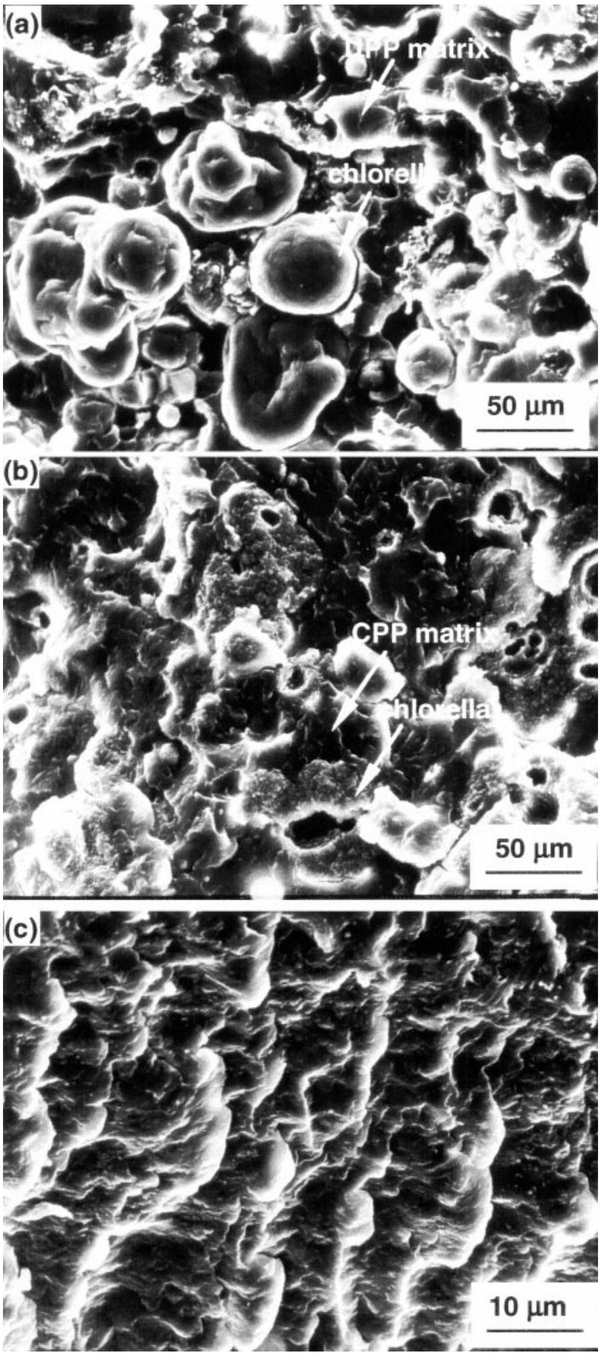


Fig. 7 Micrographs of fractures of 70UPP–30OCH blend (a), 70CPP–30OCH blend (b), and 70CPP–30GCH blend (c).

the CPP matrix occurs intensively around *Chlorella* particles (Fig. 8b).

According to this model, *Chlorella* has no influence on the properties of the UPP matrix because of the lack of interaction between *Chlorella* and UPP. The crystallinity and thus the thermal properties of the UPP matrix exhibit hardly any change after blending with *Chlorella*. Thus the tensile strength (σ_m) of a UPP–*Chlorella* blend depends entirely on the strength of the UPP matrix (σ_{upp}), and decreases with an increase in *Chlorella* content according to the relation $\sigma_{upp}A_{upp}/A$, where A_{upp} is the section area of the UPP matrix and A is the total cross-section area. This explains well the sharp drop in tensile strength of the UPP–*Chlorella* blend shown in Fig. 5. On the other hand, the tensile strength of a CPP–*Chlorella* blend depends not only on the strength of the CPP matrix (σ_{cpp}) but also on that of the *Chlorella* grains ($\sigma_{c\text{–}c}$), because of stronger interactions between MPP and *Chlorella* ($\sigma_{p\text{–}c}$) than between *Chlorella* cells: $\sigma_{p\text{–}c} > \sigma_{c\text{–}c}$. Accordingly, the σ_m value of a CPP–*Chlorella* blend is determined by the relation $\sigma_{cpp}A_{cpp}/A + \sigma_{c\text{–}c}A_c/A$, where A_{cpp} is the section area of the CPP matrix and A_c is the section area of *Chlorella* grains. This explains the marked increase in tensile strength of the CPP–*Chlorella* blend compared with the UPP–*Chlorella* blend because of the role of $\sigma_{c\text{–}c}A_c/A$, although σ_{cpp} might decrease a little because of the decrease in crystallinity of the CPP matrix after blending with *Chlorella*. Furthermore, this model is consistent with the reduction of melting and solidification enthalpies of the blend due to the increase in the amorphous phase after the CPP is blended with *Chlorella*, and with the T_g depression of the blend according to the volume expansion of the CPP matrix around *Chlorella* particles.

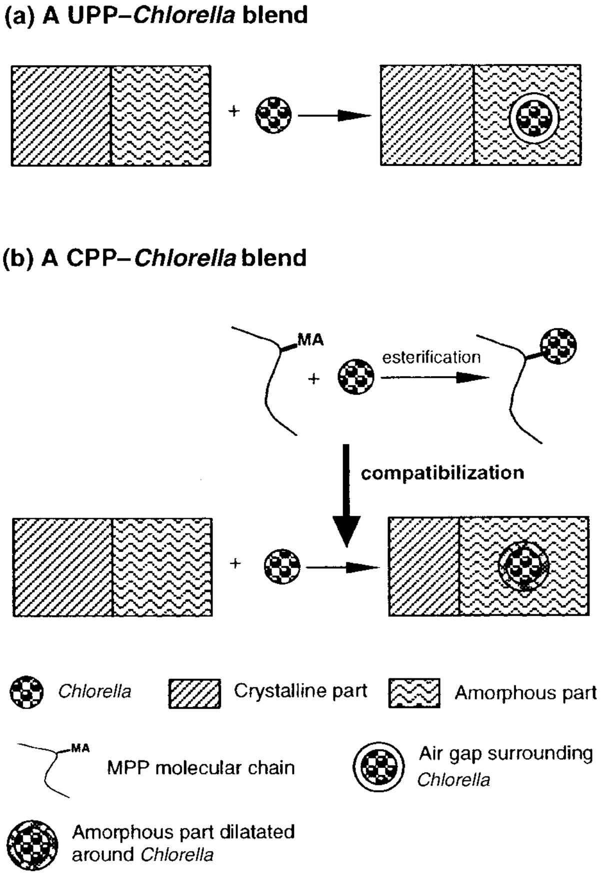


Fig. 8 A model structure for UPP–*Chlorella* blend (a) and CPP–*Chlorella* blend (b).

Conclusion

A novel blend of polypropylene (PP) with *Chlorella* has been synthesized successfully by a melt-mixing method with maleic anhydride-modified polypropylene (MPP) as a compatibilizer. The interfacial adhesion of hydrophobic PP to hydrophilic *Chlorella* is due to the formation of chemical bonds between maleic anhydride groups of MPP and hydroxy groups of *Chlorella* through solid-phase esterification. The single maleic anhydride groups have the highest reactivity with *Chlorella*. From the comparison with PP–*Chlorella* blends without MPP, the ester bonds between MPP and *Chlorella* cause a decrease in crystallinity of the MPP matrix which is the primary origin of the decrease in melting and solidification enthalpies of the MPP–*Chlorella* blend, and strongly induces expansion of the MPP matrix around the *Chlorella* particles to decrease the T_g value. Consequently, the PP–*Chlorella* blend with MPP exhibits a marked increase in tensile strength and in Young's modulus compared with the blend without MPP, because of stronger interactions between MPP and *Chlorella* than those between *Chlorella* cells.

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