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Production of Biopolymer Composites by Particle Bonding

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1. Introduction

With the rising concern for environmental protection, biodegradable polymers and biocomposites have attracted considerable attention as green materials and biocompatible materials that will replace some or all of the synthetic plastics in many applications.
Because petrochemical-based plastic material persists beyond its functional life, a waste disposal problem is facing modern society. Research to alleviate pollution and litter problems includes efforts to develop plastics that degrade more rapidly in the environment. Most of our waste is either stored in landfills or composted. Since most of the natural polymers are biodegradable, the use of natural polymers as a substitute for non-biodegradable synthetic polymers can be environmentally beneficial to some extent. Recently, many research groups have concentrated on the development of biodegradable polymer blends or composites from starch (Ma et al., 2008; Grazuleviciene et al., 2007; Gaspar et al., 2005), corn gluten meal (Samarasinghe et al., 2008; Beg et al., 2005; Wu et al., 2003a), wheat gluten (Zhang et al., 2007; Olabarrieta et al., 2006; Ye et al., 2006; Domenek et al., 2004; Kayseriliolu et al., 2003), and zein (Qu et al., 2008; Corradini et al., 2006; Wu et al., 2003b). In most cases, commercially available biopolymers contain a significant amount of unwanted materials that remain after the extraction/isolation process. Purification of these materials is very costly for the practical utilization of these agricultural products as a component of useful final products. If these agricultural excess products can be used without further purification, it can minimize the use of toxic chemicals, simplify the manufacturing process, save energy, and lower the production cost.
In this chapter, a new fabrication procedure for the production of biopolymer composites will be introduced. In this procedure, a corn protein, zein, is utilized as a binder for matrix materials (Kim, 2008). Matrix material can be chosen from both agricultural products and non-agricultural products. Composite materials fabricated from agricultural products such as starch and protein powders are biodegradable while those fabricated from non-agricultural products such as iron powder and glass spheres are not.

2. Fabrication of composites by particle-bonding

Conventionally, polymer composites had been manufactured by mixing the component materials in an extruder at high temperature. If the raw material is a mixture of various

components with impurities, phase-separation, decomposition, and gas generation will interfere with the extrusion process. A new methodology, called particle-bonding technology, was developed for the production of biodegradable/non-degradable polymer composites that will potentially replace existing petroleum-based polymers. This technique requires neither extrusion nor processing at high temperatures. Instead, micrometer scale raw materials (powders) are coated with a corn protein, zein which has a strong adhesive force, and compressed to form a rigid material. Since this technique does not require purification of raw materials, various types of compounds can be used as component materials. During the fabrication process, raw materials in powder form are bound by zein. Zein is utilized because of its good adsorption to hydrophilic surfaces and strong adhesive properties. Both the unusual behavior of zein molecules in the aqueous alcohol solution and its strong adhesive property play a major role in the fabrication process of the particle-bonding technology. Mechanical properties such as compressive yield strength, modulus of elasticity, and yield strength at 0.2% offset of the fabricated polymer composites confirm the validity of the presented process.

3. Characteristics of zein

3.1 Source

Commercial zein is essentially a by-product of the corn wet-milling industry. In the wet milling process, steeped corn in water is milled to separate the hulls and germ from the endosperm, which is further milled into a fine slurry. Centrifugal separation of starch from the endosperm slurry leaves a protein-rich mass, i.e., corn gluten meal, from which zein is extracted (Padua & Wang, 2002). Annual zein production in the U.S. is more than 1 million pounds, mostly used in formulations of specialty food and pharmaceutical coatings (Shukla, 1992; Lawton, 2002).

Biologically, zein is a mixture of proteins varying in molecular size and solubility. These proteins can be separated by differential solubilities and their related structures into four distinct types: α, β, γ, and δ (Coleman and Larkins, 1999). α-Zein is the most abundant, accounting for ca. 70% of the total (Thompson and Larkins, 1989). The next most abundant zein is γ-zein, contributing ca. 20% to the total. α-Zein can be extracted using only aqueous alcohol, whereas the other zeins need a reducing agent in the solvent to be extracted (Lawton, 2002). α-Zein that is extracted with a reducing agent shows up as two bands with apparent migration rates of 19 and 22 kDa on SDS-PAGE (Coleman and Larkins, 1999). Commercial zein is made up of α-zeins (Wilson, 1988).

Zein can be used as a biodegradable material (Shukla & Cheryan, 2001; Lawton, 2002), and as early in 1909, it was used to prepare plastics (Goldsmith, 1909). Later, the related research was delayed due to the emergence of petroleum-based plastics. However, within the last two decades, zein has again attracted attention because of its biodegradability.

3.2 Solution behavior

Zein's defining characteristic is insolubility in water except in the presence of alcohol, high concentrations of urea, high concentrations of alkali (pH 11 or above) or anionic detergents. This is due to its amino acid composition. Zein is particularly rich in glutamic acid (21–26%), leucine (20%), proline (10%) and alanine (10%), but deficient in basic and acidic amino acids. The high proportion of nonpolar amino acid residues and deficiency in basic and acid amino acids is responsible for the solubility behavior of zein. (Shukla, 1992)

Conventionally, aqueous ethanol has been used as a solvent for zein in many experiments (Parris and Coffin, 1997; Fu and Weller, 1999; Lawton, 2002; Dickey et al., 2003; Kim et al., 2004; Guo et al., 2005). It is one of the good solvents for zein (Manley and Evans, 1943). Although it is known that 60–95% ethanol content is adequate for solubilization of zein, the effect of variation of alcohol content on the behavior of individual zein molecules has not been well understood until 2008. Fu and Weller (1999) reported on the rheology of zein solutions in aqueous ethanol. Zein (2–12%) in 50%, 60%, 70%, 80%, and 90% aqueous ethanol was investigated. Regardless of zein concentration, the overall trend showed that the viscosity of the solution decreased as the concentration of ethanol increased from 50% to 90%. This result indicates that the apparent molecular weight of zein decreases at a higher ethanol content. Yamada et al. (1996) reported that zein films prepared from 80% (v/v) aqueous ethanol did not show enough waterproof property compared with those prepared from 70% (v/v) aqueous acetone. In addition, aggregate formation was observed in both films. Dong et al. (2004) reported that SEM revealed that the zein film prepared from 70% ethanol was composed of particles of diameter 100–500 nm. These particles were agglomerated to form a film. The concentration of zein had no significant effect on particle size. Guo et al. (2005) used atomic force microscopy (AFM) for the visualization of zein globules formed from 70% (v/v) aqueous ethanol on the surface of mica. Depending on the concentration of zein in the solution, the diameter of globules ranged between 150 and 550nm, or between 60 and 120nm. If we compare zein with other proteins of similar molecular weight, the diameter of a zein molecule is expected to be ca. 5 nm (Cantor & Schimmel, 1980). Therefore, the data from previous researches clearly indicate that zein forms aggregates with a very large aggregation number in aqueous ethanol.

4. Particle bonding technology

4.1 Aggregation of zein in aqueous ethanol

The developed particle-bonding technology makes use of the aggregate-forming tendency of zein in aqueous ethanol solution. Although the traditional solvents for zein, 70–90% aqueous ethanols, did not show much difference in terms of the capability of making solutions, transmittance measurement showed there is a variation of aggregate size depending on the ethanol content in the solvent mixture (Kim & Xu, 2008). Transmittance of zein solutions was measured at several zein concentrations with a turbidimeter that is composed of a 633nm He–Ne laser, temperature-controlled sample block, stirrer, neutral density filter, and a laser power meter. Zein solutions of 0.2%, 0.5%, 1%, and 2% (w/w) were examined with a turbidimeter to find the best solvent composition (Fig. 1). The data show a peak of transmittance at around 90% aqueous ethanol but the transmittance dropped with a higher concentration of ethanol. However, although there was variation in the transmittance in the range of 70–90%, no precipitation was observed. It is an indication that there is a size variation of zein molecules as the percentage of the ethanol changes. Since the transmittance variation was too dramatic to be considered as due to a change in the individual molecular size, it was expected that there is a growth of particle size by aggregate formation of individual zein molecules. For further understanding of the aggregation behavior of zein in aqueous alcohol solution, the size variation of solute was investigated by a dynamic light scattering (DLS) technique. At greater than 90% ethanol, unlike the case of 70-90% ethanol solution, precipitation was observed and time-dependent transmittance was observed. The reason for the dramatic change in the transmittance in the narrow region at around 90% ethanol could only be explained after obtaining data from DLS experiment.

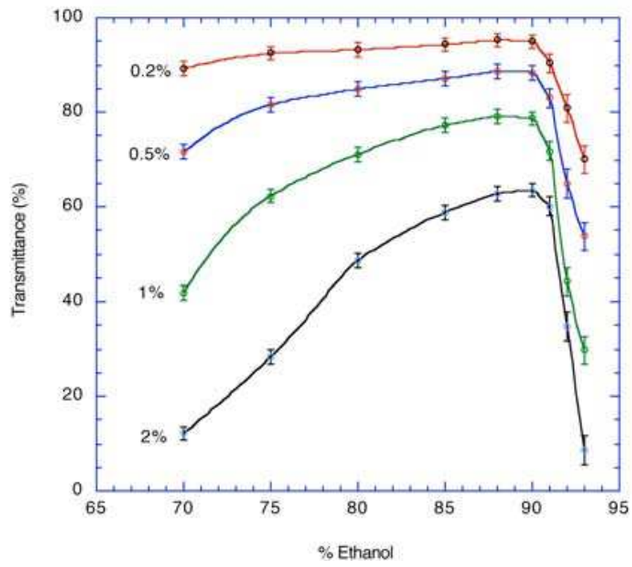

Fig. 1. Transmittance of zein in a series of ethanol solutions. Zein solutions (0.2–2%) were examined at 25.0 ± 0.1 °C. A 10mW He–Ne laser (λ = 633 nm) was used as a light source.

For the measurement of the degree of aggregation of zein in various ethanol/water mixtures, a DLS experiment was performed with an autocorrelator and a goniometer equipped with an argon laser (λ = 514.5 nm). All experiments were carried out with 0.1% (w/w) zein solution at 25.0 ± 0.1 °C. The scattered intensities were determined by using the standard photon counting method. Hydrodynamic radii of zein aggregates were obtained as follows. The DLS experiment yields a correlation function given as

$$g^{(1)}(t) = \exp(-\Gamma t) \tag{1}$$

where $\Gamma = D_t q^2$ (Johnson and Gabriel, 1994). From the slope of q^2 vs. Γ plot, we obtain a diffusion coefficient of a solute molecule, D_t. Here, q is the scattering wave vector. The hydrodynamic radii of aggregates can be calculated by the Stokes–Einstein relationship

$$R_h = (kT)/(6\pi\eta D_t) \tag{2}$$

where k is the Boltzmann constant, T is the absolute temperature (K), η is the viscosity of the solvent (P), and D_t is the diffusion coefficient (cm^2/s).

Fig. 2 shows dimensional variation of hydrodynamic radii of zein aggregates in aqueous ethanol solutions. At around 90% ethanol, a sharp decrease and increase in the hydrodynamic radius of zein was observed. The volume of the aggregates was calculated assuming the aggregates are spherical. As the molecular weight of zein is known from the SDS-PAGE experiment (Cabra et al., 2005; Padua & Wang, 2002), the size of single molecule was estimated from the list of proteins (Canton & Schimmel, 1980). Although it is not practically possible to obtain the data for the hydrodynamic radii for all ethanol/water compositions, it is probable that each zein molecule exists as a freely moving individual particle at around 90% ethanol. The most probable hydrodynamic radius of single zein molecule was assumed at 89.7% ethanol. Including this conjectured data point, the overall trend of the variation of the volume of aggregates is shown by the red line in Fig. 2. The volume of each aggregate and the degree of aggregation were calculated by assuming the

specific volume to be close to one. The degree of aggregation of zein was gradually decreased when the composition was changed from 70% to 90% ethanol. At around 90% ethanol solution, the aggregation number was at the minimum. After that, the aggregation number increased dramatically in the solvent composition higher than 90% ethanol. The overall behavior of aggregate formation of zein suggests that there is a structural change in the conformation of zein aggregates at around 90% ethanol. Since the amphiphilic behavior of zein has been known (Wang et al., 2004a & 2004b), this behavior can be interpreted as the inversion of micellar structure of zein aggregates as the solvent composition changes from a hydrophilic environment to a more hydrophobic one. According to the aforementioned aggregation behavior of zein, the structural inversion of zein can be induced by increasing or decreasing the composition of ethanol from 90%.

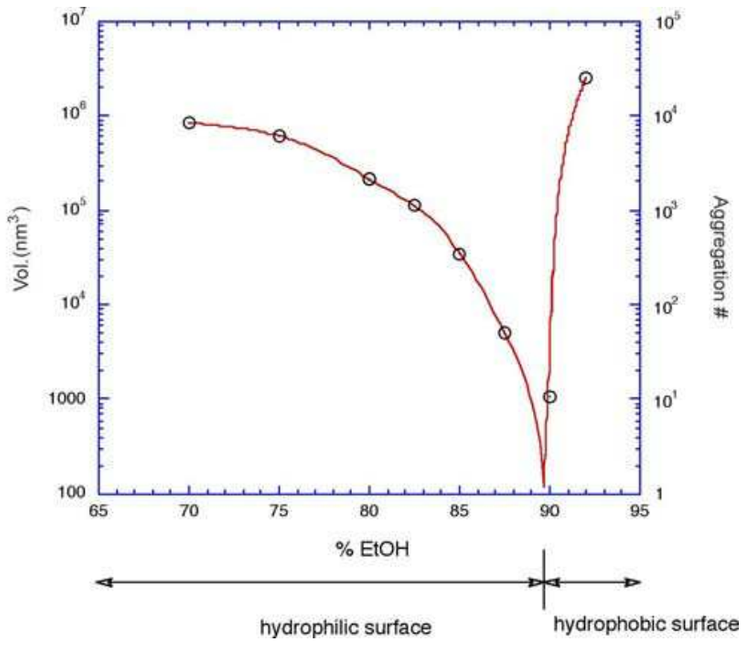

Fig. 2. Dimensional variation of zein aggregates in a series of ethanol solutions. Data were obtained by a dynamic light scattering instrument equipped with an argon ion laser (λ = 514.5 nm). The experiment was carried out with 0.1% (w/w) zein solution at 25.0 ± 0.1 °C.

4.2 Amphiphilic nature of zein

If each zein molecule behaves as an amphiphile, it is expected that zein molecules form a macromolecular micelle—globular aggregates with the hydrophilic moiety exposed to the surface and hydrophobic moieties clumped together in the aqueous ethanol with up to 90% ethanol content. 90% aqueous ethanol should be the best solvent for zein as the aggregation number was at its minimum (Fig. 2). As the percentage of ethanol increases to higher than 90%, the solvent medium turns more hydrophobic and a different type of macromolecular micelle will be formed. This time, the hydrophobic moiety will be exposed to the surface and hydrophilic moieties will clumped together. In other words, the orientation of each molecule in the micelle will be reversed.

The structural inversion of zein molecules or aggregates had been suggested by Yamada et al. (1996) when they found that the hydrophobicity of zein film depends on the type of

solvent system used for its preparation. This observation supports our view that the inversion of micelle-like structure of zein aggregates occurs at around 90% ethanol. The micelle-like structures formed in lower than 90% ethanol have hydrophilic moieties that are oriented toward the solvent medium. In this case, the surface charges of particles repel each other without precipitation whereby they form a turbid solution. On the other hand, the micelle-like structures formed in greater than 90% ethanol have hydrophobic moieties that are oriented toward the solvent medium. In this case, the particles attract each other by van der Waals force so that aggregation, followed by precipitation, is induced. This behavior indicates that the micelles formed in this ethanol content have no or negligible charges on the surface whereby van der Waals force between aggregates can play a major role in the formation of precipitates. Micelle formation of zein in aqueous ethanol is schematically illustrated in the top row of Fig. 3 (no added substrate particles). Considering the micelle formation of surfactants at above CMC (Critical Micelle Concentration), the simplified model for the aggregation of zein molecules is conceivable. Inclusion of the experimental result shown in Fig. 2 readily yields inversion of micelle at around 90% aqueous ethanol. This behavior resembles pH-induced inversion of micelle that was formed by diblock copolymer unimers (Wang et al., 2006). It is expected that zein molecules would surround hydrophilic or hydrophobic particles depending on the percentage of ethanol in the solution. The schematic presentation of this behavior is shown in the bottom row of Fig. 3 (with added

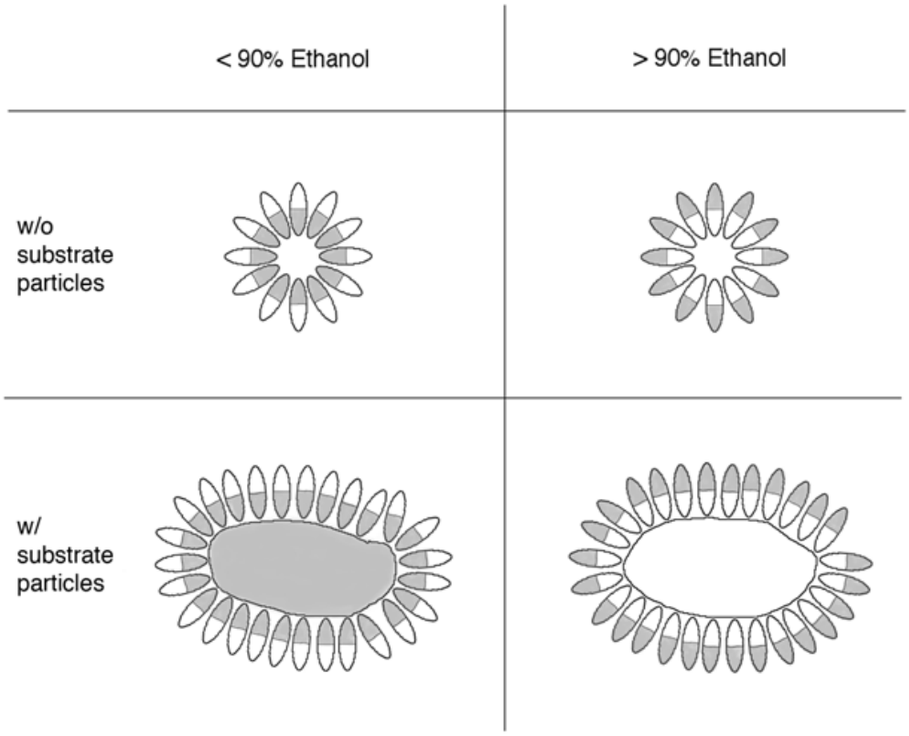

Fig. 3. Schematic diagram of the structural inversion of micelle-like structured zein molecules with and without added substrate particles in aqueous ethanol solutions. Shaded areas represent hydrophobic surfaces. When particles with hydrophilic (hydrophobic) surfaces are mixed with zein molecules, their surfaces will be surrounded by zein molecules with hydrophilic (hydrophobic) moieties oriented toward their surfaces.

substrate particles). This viewpoint is again supported by a simple experiment as follows. According to Fig. 2, addition of ethanol or water to a zein solution in 90% ethanol will induce larger aggregates. If two kinds of particles, one with hydrophilic surface and the other with hydrophobic surface, are dispersed in this system (zein in 90% ethanol solution), depending on the added solvent, ethanol or water, zein molecules would surround only one of the two particles. The aggregate formation of zein was experimentally observed with the above-mentioned procedure where glass spheres were employed as particles with hydrophilic surface and toner with hydrophobic surface. The sizes of the two particles were similar to each other and the color of the glass spheres was white while that of toner was black (Fig. 4).

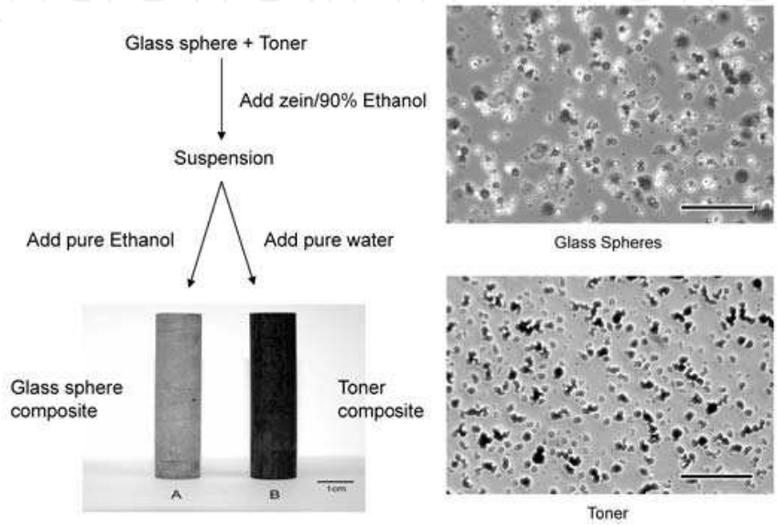

Fig. 4. Composite materials prepared from a mixture of glass spheres and toner. The selective adhesion of zein molecules to the surfaces of hydrophilic (glass spheres) or hydrophobic particles (toner particles) allows us to prepare a glass sphere composite (A) or a toner composite (B) from their mixture. 100 μm bars are shown in the microscopic images.

In this demonstration, 10% zein in 90%ethanol mixed with hydrophilic particles (glass spheres, o.d. = ca. 10 μm) and hydrophobic particles (toner, o.d. = ca. 10 μm) was prepared. When ethanol was gradually added to the solution, zein surrounded the glass spheres and formed a large agglomerate while the toner particles were minimally affected. The surface of precipitated zein is so sticky that the glass spheres coated with zein stick together and form large agglomerates. During this time, some of the toner particles, although they are not coated with zein, are physically embedded in the agglomerates. That is why the color of glass spheres is not pure white. The same reasoning applies to the toner composites. As the agglomerate was compressed in the cylindrical mold, a glass sphere composite was produced (Fig. 4). Since a phase contrast microscope was used for taking images in the inset of Fig. 4, some particles of glass spheres look black. On the other hand, when water was added to the solution, zein surrounded the toner particles and formed small agglomerates while the glass spheres were not affected. Smaller agglomerates than those of the previous case were formed because of the surface charges of particles that repel each other. A toner composite was produced as the agglomerate was compressed in the cylindrical mold (Fig. 4). In this experiment, the behavior of zein in the latter case is similar to that of detergents in a washer. Toner particles are nonpolar and insoluble in water. When detergents and

hydrophobic particles (e.g., toner or oily dirt) are mixed in water, the hydrophobic moiety of detergent molecules are attracted to the surface of hydrophobic particles. The micelle-like structures formed by this mechanism contain hydrophobic particles in the center. By the same reasoning, if some amphiphiles (e.g., zein) and hydrophilic particles (e.g., glass spheres) are dispersed in a hydrophobic medium, the hydrophilic moiety of zein molecules will be attracted to the surface of hydrophilic particles. The above experimental result supports the concept for the structural inversion of micelle-like zein molecules. As stated above, addition of more ethanol to a zein solution in 90% ethanol induces large aggregates. It is the basis of the procedure developed in our lab for the production of polymer composite materials.

4.3 Principle of fabrication

The particle bonding technology makes use of the powerful adhesive properties of zein to bind the matrix materials. The adhesive properties of zein had not been recognized for a long time until recent research by Parris and Dickey (2003). The enormous bonding strength of zein could easily be demonstrated by using zein as a glue; zein solution prepared in organic solvent mixture (CH_2Cl_2/MeOH; 60/40) was applied on the surface of wood blocks (Uy, 1998). After 24 h, when the bonded wood blocks were taken apart, bonded parts were more difficult to break apart than the original wood block.

The surface of most matrix materials prepared from agricultural commodities is hydrophilic. At greater than 90% aqueous ethanol solution, the hydrophilic moiety of zein molecules should have a tendency to find hydrophilic materials in its solution and adsorb on its surface to hide the hydrophilic moiety and externally expose the hydrophobic moiety. In this situation, when matrix materials with hydrophilic surfaces, e.g., most of the biopolymers, are mixed with zein, the latter will be adsorbed on the surface of the former. As a result, we obtained matrix materials coated with zein molecules. Consequently, large agglomerates are formed because of the adhesive character of zein in the mixture. When these agglomerates are squeezed in the mold, the solvent is removed and a lump of protein composite is obtained.

There is a fundamental difference in the behavior of aggregates between the particles with hydrophilic surface and those with hydrophobic surface. In the case of the particles with hydrophobic surface, they form larger agglomerates by dispersion force between particles as soon as they are formed. Therefore, these particles are very unstable in the solution and form larger particles until they precipitate. The aggregation process is readily observed every time when the biopolymer composites are fabricated. On the other hand, the particles with hydrophilic surface do not spontaneously form larger agglomerates because of the electrostatic repulsion between particles.

The first step of the fabrication process is to disperse the matrix material and zein in ethanol. Only a small amount of ethanol that will barely immerse the matrix material is enough at this stage. The matrix material must be a powder of micrometer-scale particle size, and most of the spray-dried biopolymers satisfy this condition. The second step is to dissolve zein in the mixture by adding a calculated amount of water to make the composition of the solvent mixture to be ca. 90% aqueous ethanol. Enough time (typically 2-3 min) should be allowed for zein molecules to fully dissolve in the solution. From this point, depending on the hydrophilicity of the matrix material, the fabrication procedure needs to follow a different process.

In the case of hydrophilic powders, ethanol is added to make the ethanol content of the solvent mixture greater than 95%. At this moment, zein molecules are adsorbed to the surface of the

matrix particles, and the sticky characteristics of zein induce agglomeration of the particles. The final step is to squeeze out the solvent mixture from the chunk material in the mold.
In the case of hydrophobic powders, water is added to make the ethanol content of the solvent mixture less than 95%. At this moment, zein molecules are adsorbed to the surface of the matrix particles, but the charges on the surface of proteins prevent the particles from binding together. To obtain aggregated form of particles, the suspension needs to be filtrated to remove the solvent mixture. An alternative choice is to add salts in the solvent mixture to screen the charges on the surface of protein molecules that are surrounding particles. The principle of this procedure is the same as that of "salting out" in colloid chemistry. The final step is to squeeze out the solvent from the chunk material in the mold.

4.4 Fabrication procedure - example

4.4.1 Particles with hydrophilic surface

Composites can be prepared by using molds fabricated from Teflon and aluminum. Typical procedure is as follows (example for composites with 20% zein). Both 6 g of matrix material and 1.5 g of zein powder are dispersed and mixed thoroughly in 13.5 g of absolute ethanol in a plastic container. Then 1.5 g of distilled water are added and stirred until the zein is fully dissolved (2–3 min). After that, 50 g of ethanol are added with vigorous stirring. During this time, particles aggregate to form a large chunk. Excess aqueous ethanol is decanted, and the aggregate is poured into a Teflon mold. Compression pressure is maintained at 75 lbs/cm^2 for 2 min. The fabricated specimens are air-dried at least for 72 h. For the measurement of mechanical properties, test specimens are fabricated by the method specified in the above and the content of zein are calculated by (wt. of zein)/(wt. of both matrix and zein) x 100. If the density of matrix material is very low, more than 15 g (ethanol 13.5 g + water 1.5 g) is needed for dispersion because of its large volume. In that case, the amount of the second addition of ethanol (50 g) needs to be adjusted accordingly. If n times larger composites need to be fabricated, the above procedure needs to be modified by simply multiplying the amount of the materials and chemicals by n times.

4.4.2 Particles with hydrophobic surface

In the case of particles with hydrophobic surface, both 6 g of matrix material and 1.5 g of zein powder are dispersed and mixed thoroughly in 13.5 g of absolute ethanol (example for composites with 20% zein). Then 1.5 g of distilled water are added and stirred until the zein is fully dissolved. Fabrication procedure up to this stage is the same as that of hydrophilic particles. After that, 50 g of water are added with vigorous stirring. During this time, unlike as in the hydrophilic particle case, particles do not spontaneously aggregate to form a large chunk because of the surface charges of each zein-coated particle. By adding a small amount of sodium chloride solution, agglomeration/precipitation will be induced. The rest of the procedure is the same as that of hydrophilic particle case.

4.5 Mechanical properties

As far as the size of the particle that will be suspended is not too large, any type of particles can be used for the base materials of polymer composites. As a test system, a wheat protein mixture, gluten, was used as a matrix material for the fabrication of biopolymer composite. From the preliminary examination of the procedure, it was found that too little or too great of an amount of zein yields a mechanically weak product. To know the optimum amount of

zein necessary to produce the sturdiest material, the percentage of zein was varied in 8 compositions (4%, 8%, 12%, 16%, 20%, 22%, 24%, and 32%), and the compressive strengths of the product specimens were examined.

A typical compressive stress–strain diagram of gluten composite is shown in Fig. 5. In general, maximum compressive stress increased monotonously until the content of zein reached 20–22%. Repeated experiment revealed that there is a variation in the overall profile of the compressive strain vs. stress curves, but the maximum strength was always obtained with 20–22% zein, at which composition the compressive strength was comparable to that of polypropylene (Northolt, 1981). Further increase in zein content lowered the maximum compressive stress.

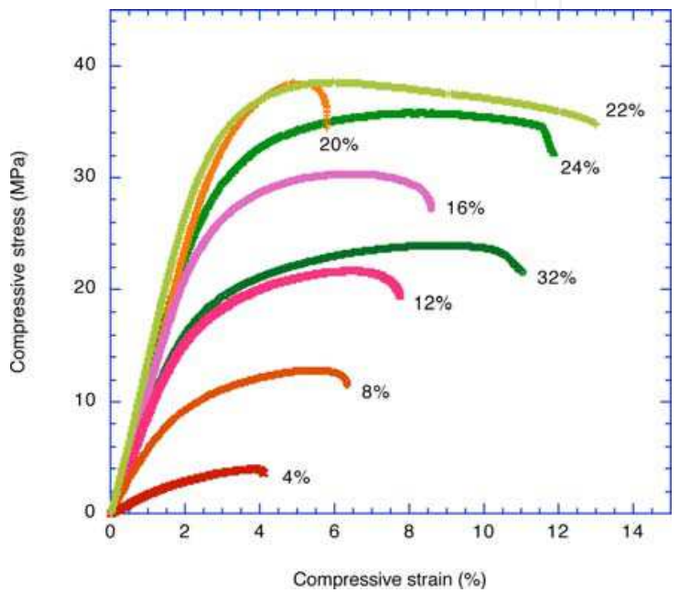

Fig. 5. Mechanical property of gluten (wheat protein) composites. Effect of the percentage amount of zein was demonstrated. Test was performed by ASTM standard, D695.

The compressive yield strength, modulus of elasticity, and yield strength at 0.2% offset are plotted as a function of percentage of zein to find the optimum composition of zein (Fig. 6). These three mechanical properties show the same trend, i.e., mechanical strength reaches its maximum when around 22% of zein is included in the composite. This experimental result clearly demonstrates that 20–22% is the optimum composition of zein in the case of gluten composite.

Processing pressure is another variable that determines the strength of the final product. Its effect was investigated by varying the pressure that is applied to the mold during the process. Fig. 7a shows that the overall stress–strain curve profile does not change at various processing pressures. To obtain an overview of the pressure effect, compressive stress at 10% strain was plotted as a function of processing pressure in Fig. 7b. This graph demonstrates that the mechanical strength of the composites monotonously increases as greater pressure is applied to the mold in the tested pressure range. In addition, it shows that the composite has a base strength even without applied pressure to the mold. According to this data, the strength of the composite will be doubled at a processing pressure of 150 lb/cm^2.

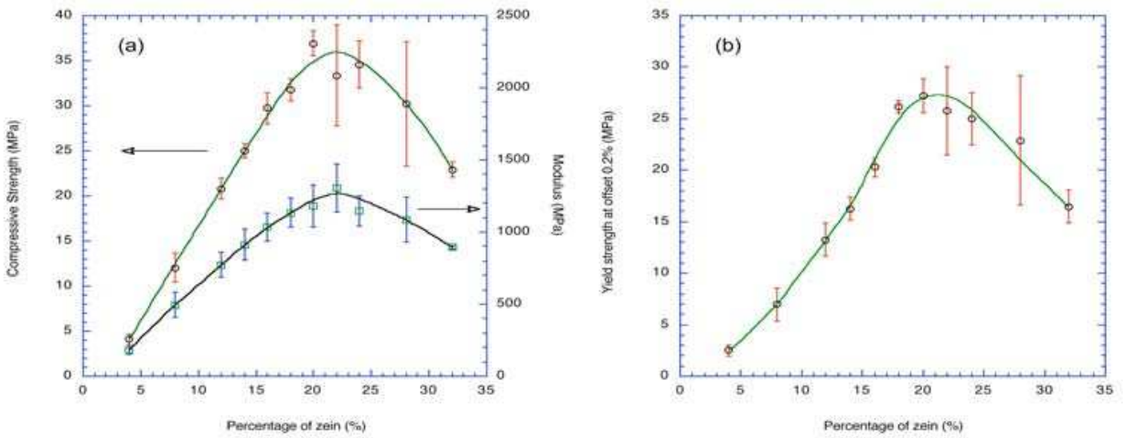

Fig. 6. Effect of the percentage of protein adhesive on compressive modulus, compressive strength, maximum load, and yield strength at 0.2% offset. (a) Composition vs. compressive modulus and compressive strength. (b) Composition vs. yield strength at 0.2% offset.

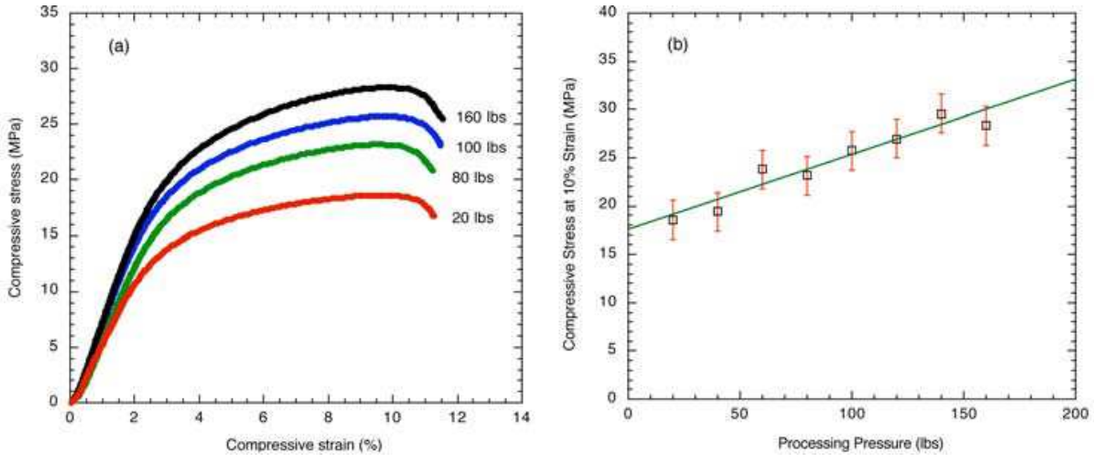

Fig. 7. Processing pressure effect. (a) Stress–strain curve at various processing pressure. (b) Compressive stress at 10% strain was plotted as a function of processing pressure. The cross section of the mold was 1.33 cm². For this experiment, the composition of zein was fixed to 15%.

In order to show that the fabrication of polymer composite from hydrophilic particle and zein is a universal behavior, glass spheres were used as a matrix material. The percentage of zein was varied from 4% to 28% and the mechanical strengths of the fabricated glass sphere composites were measured. Fig. 8 shows the compressive strain vs. stress curves obtained from glass sphere composites. The strength of the composites increased until the composition reached 24% and was weakened thereafter. It is noticeable that the maximum strength of glass sphere composites is reached in less than 3% compressive strain, while that of gluten composites is as high as 20% (Fig. 5). This discrepancy should be caused by the difference in the hardness of the constituent particles.

The current processing technique uses controlled precipitation to coat particles of biopolymers with a binder, zein, to form a microcomposite, and then consolidating the material in a compression molding process. Therefore, it can be used with any type of

materials that does not dissolve in ethanol. Most proteins and carbohydrates belong to this category. Mixtures of two or more compounds can also be used for the production of polymer composites.

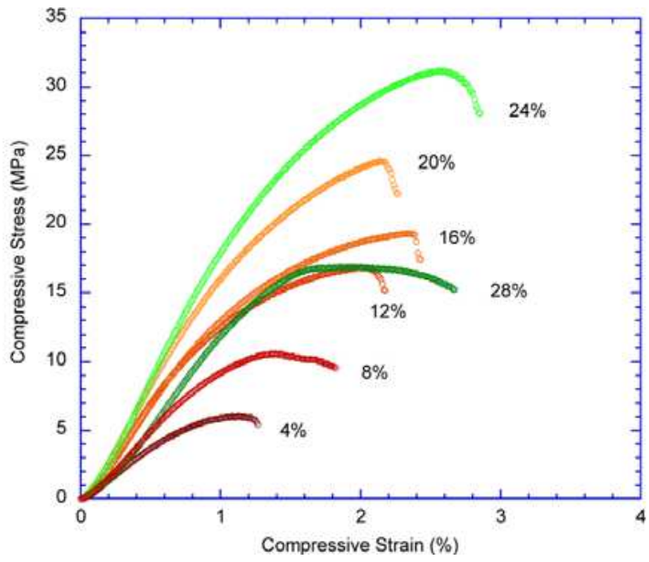

Fig. 8. Mechanical property of glass sphere composites. Effect of the percentage amount of zein was demonstrated.

The compressive strength of the composite produced from cellulose is a little weaker than that from gluten. When composites are manufactured from the mixture of these two materials, it is expected that the strength of the composite becomes weaker as the content of cellulose is increased in the mixture. Fig. 9(a) demonstrates that the incorporation of weaker matrix material weakens the strength of the composite. For this experiment, sample composites were manufactured from 80 wt.% matrix material mixture and 20 wt.% zein. The weight fraction of cellulose in the abscissa of Fig. 9(a) denotes wt.% of cellulose in the mixture of the two matrix materials. This observation indicates that the strength of the composite relies on the hardness of the constituent particles. In this example, the sizes of the matrix particles are not much different from each other, as shown in the inset of Fig. 9. On the other hand, when the particle sizes are very much different from each other as in the case of the mixture of gluten and cornstarch, somewhat different result was observed. The compressive strength of composite produced from cornstarch was a little weaker than that from gluten as well. As these two materials, gluten and cornstarch, were mixed together, the highest strength was observed when 40% starch was incorporated in the mixture (Fig. 9(b)). This behavior was interpreted as follows. Gluten powders are composed of larger particles than those of cornstarch. The strength of the composites originates from the strength of the individual particles. When the composites were fabricated at the same condition, the compressive strength of gluten composite (30 MPa) was higher than that of cornstarch composite (23 MPa). When the two materials are mixed together, the small cornstarch particles will fill the gaps between large gluten particles. For up to 40% cornstarch composition, the reinforcement offered by cornstarch plays a role. Once all the gaps are filled with cornstarch, the excessive cornstarch which is weaker than gluten degrades the strength of the final product.

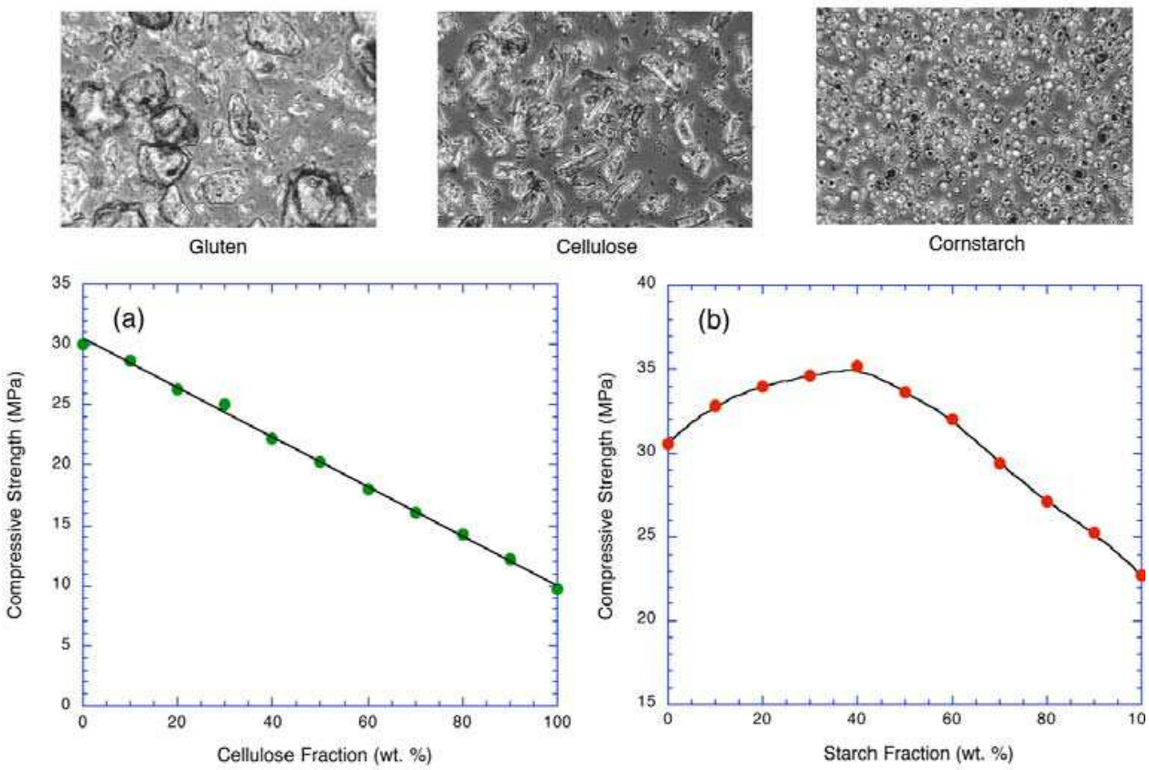

Fig. 9. Effect of incorporation of second component (cellulose (a) and starch (b)) into the gluten composites. Compressive strength was monitored as the content of second component was increased. Each composite contains 20% (w/w) zein. Microscopic images of gluten, cellulose and cornstarch and are also shown.

To show that the aforementioned technology can be applied to most of the biopolymer particles, various type of materials were used to fabricate the composites (Fig. 10). Some of

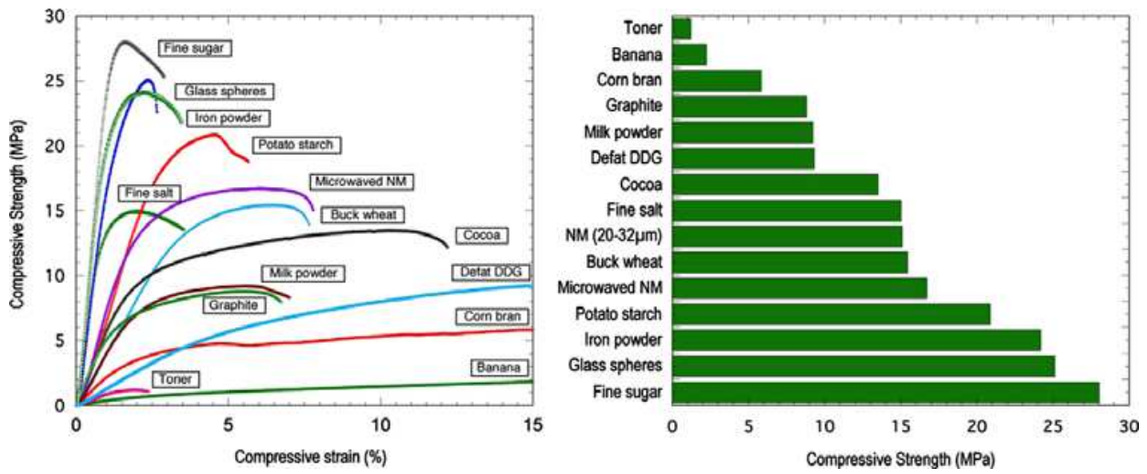

Fig. 10. Compressive stress–strain diagram of various biopolymer samples. Each composite contains 20% (w/w) zein. This illustration shows that various materials can be used for the production of polymer composites by using the particle-bonding technology.

the materials such as fine sugar, glass spheres, iron powder, fine salt, and graphite are not polymers. Since the suspension medium of the matrix material(s) contains equal or higher than 90% ethanol, matrix materials that dissolve in ethanol cannot be used. Other requirements of the particles to be used for fabricating composites are the micrometer-scale size and hydrophilicity of the particle surface. As particles with hydrophobic surface are rare, only toner was used as an example. In this case, unlike the case with hydrophilic surface, the particles were coated with zein by lowering the concentration of ethanol.

4.6 Conductive composites

As any type of particles can be used for the production of composites with the proposed technology, a conductive filler, graphite, was incorporated into the gluten composite to fabricate conducting polymer composites (Kim et al., 2010). For the presentation of the data, resistivity which is the inverse of conductivity was used as a unit for comparing the conductance of fabricated composites. It is defined as,

$$\rho = RA/L \tag{3}$$

where ρ is the resistivity (Ω-cm), R is the electrical resistance (Ω), L is the length (cm), and A is the cross-sectional area (cm^2).

By common sense, it is predictable that the more added conducting fillers, the higher the conductance of the produced composites. Fig. 11a clearly shows this trend, i.e., as more graphite was incorporated in the gluten composite, lower resistivity was observed. On the other hand, the amount of zein did not affect the resistivity of the composites. Fig. 11b is the same plot as Fig. 11a but showed the resistivity as a function of the percentage of incorporated graphite. The resistivity decreases as the percentages of graphite gets higher, but the variation of the resistivity at high percentages of graphite is not so dramatic. This decrease in the resistivity can be explained by the percolation theory (Pike & Seager, 1974; Vilcakova et al. 2002). The mechanical strength of the conducting composites was measured with the same samples as used for Fig. 11a and b. Although the percentage of zein does not affect the conductance of the composites, it does with mechanical strength as is expected. As

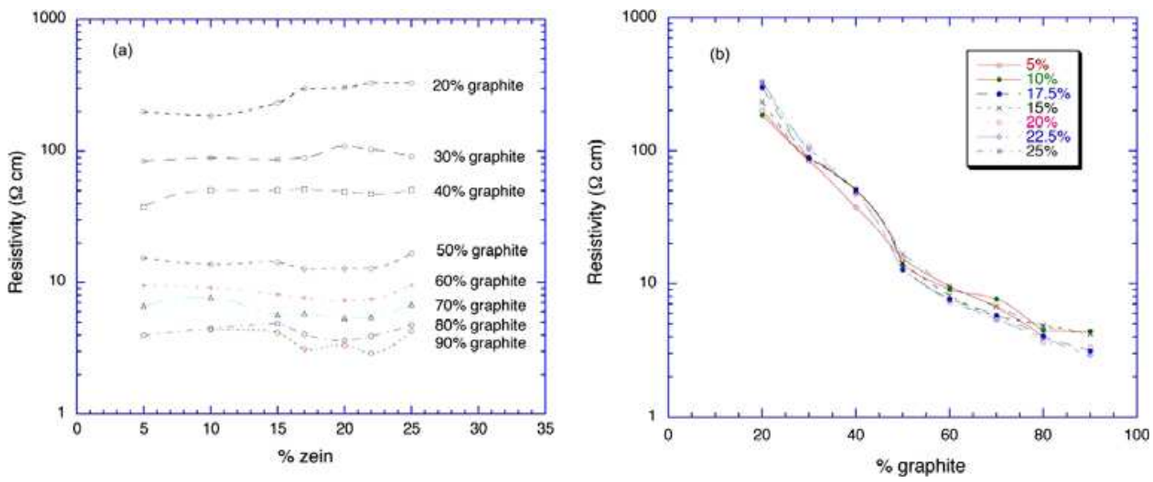

Fig. 11. Resistivity of conducting polymer composites. (a) Effect of the percentage of zein. (b) Effect of the percentage of incorporated graphite.

in the case of previous gluten composites, the strength increases until zein content increases to 22%. After that, a decrease in the mechanical strength was observed (Fig. 12a). Therefore, 22% zein is the optimum composition for this system.
Also, it was found that the inclusion of graphite weakened the mechanical strength. This trend was clearly shown again in the replot version (Fig. 12b). According to this data, the surface of graphite is not hydrophilic enough to be bound firmly with gluten particles. For this reason, the mechanical strength and conductance of graphite/gluten composite have to be compromised.

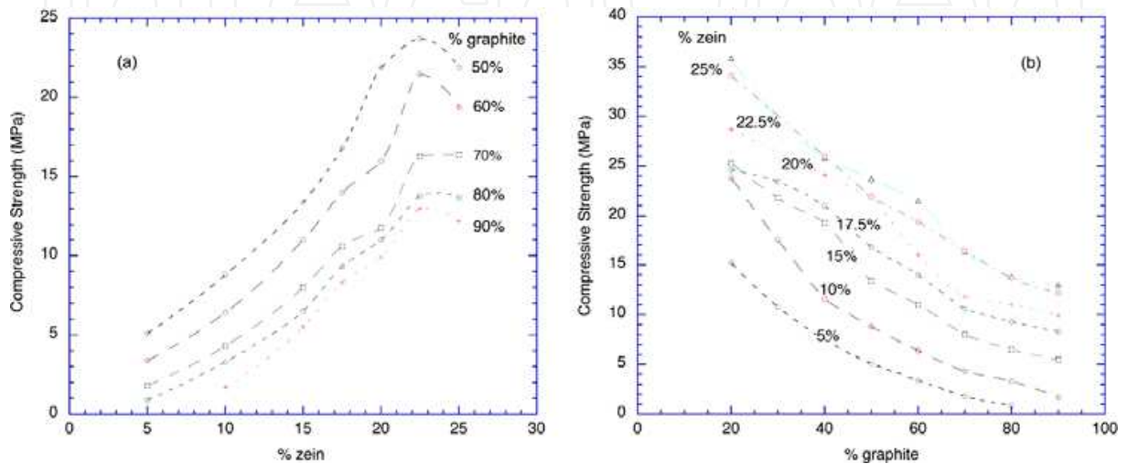

Fig. 12. Mechanical strength of conducting polymer composites. (a) Effect of the percentage of zein. (b) Effect of the percentage of incorporated graphite.

5. Future research

Although the fabrication of the composites makes use of the amphiphilic nature of zein molecules, the detailed structure of the individual molecule is not known yet. Several models have been proposed for the 3D shape of α-zein (Argus et al., 1982; Garrett et al., 1993; Tatham et al., 1993; Matsushima et al., 1997; Bugs et al., 2004; Forato et al., 2004). Despite all these trials, a generally accepted axial ratio of the individual molecule has not even been obtained yet. In this situation, discussion on the local hydrophilicity of the surface of each molecule is premature. Crystallography of zein, however, would give us a clear picture on the distribution of both polar and non-polar amino acids on the surface of each zein molecule.
Like zein, gliadin in wheat belongs to the characteristic class of proteins known as prolamines, which occur specifically in cereals (Shukla & Cheryan, 2001). Therefore, the solvent behaviour of gliadin is expected to be similar to that of zein. This point of view was examined with several instruments and supported by preliminary data. The only major difference was that the best ethanol composition for the solubilization of gliadin is 65 wt% ethanol while that of zein is 90 wt% ethanol. Preliminary data from the measurement of mechanical strength at various gliadin content is shown in Fig. 13. It is clearly shown that composite fabricated with ca. 20% gliadin is the sturdiest and the mechanical strength of gliadin composite is compatible with that of zein composite. Since the production cost for gliadin is much lower than that of zein ($0.50-1.00/lb vs. $5-10/lb), gliadin is a promising material.

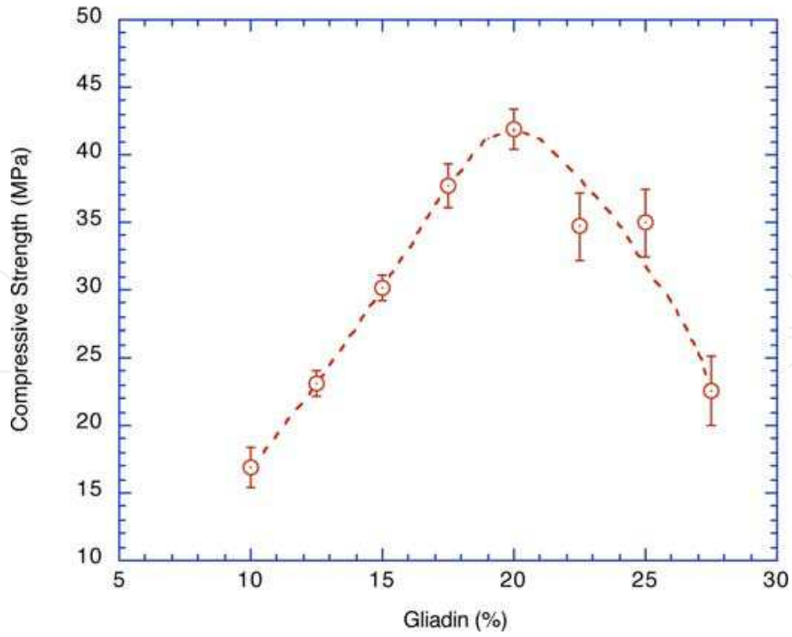

Fig. 13. Mechanical strength of composites fabricated with glass spheres and gliadin.

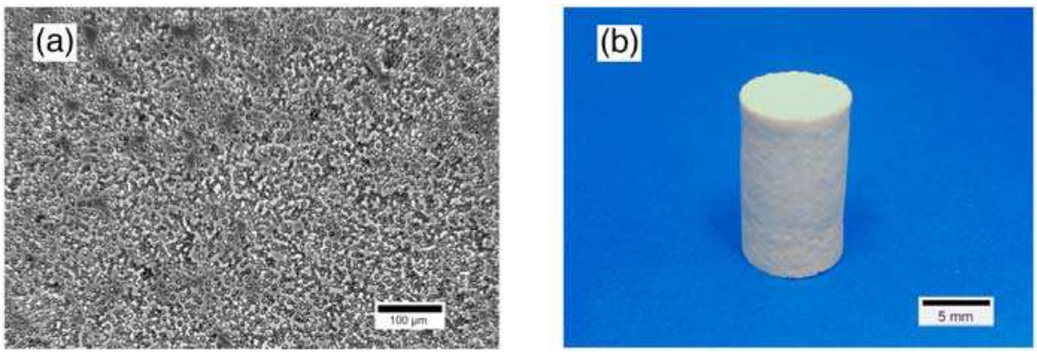

Fig. 14. Fabrication of composite with a living microorganism, yeast. (a) yeasts bearing toxin. (b) fabricated yeast pellet before cutting.

6. Conclusion

The particle bonding technology described in this chapter has the following merits.

a. It does not require purification of raw materials, except zein, thus reducing the use of chemicals and processing time.
b. Since the fabricating process is performed at room temperature, it does not require heating.
c. Biodegradable composites can be fabricated when biopolymers are used as raw material.
d. Products with compressive yield strength comparable to that of petroleum-based polymers can be fabricated.
e. In the case of the composite made with gluten, the compressive strength was comparable to that of polypropylene.

f. Any type of micrometer-scale powder that does not dissolve in alcohol can be processed.
g. Two or more types of raw materials can be used at any mixing ratio.
h. It allows for easy coloring of the product by addition of food dyes during the process.
i. Compressive strength can be adjusted by varying the processing pressure.
j. It allows the incorporation of fibers to improve the strength of the product. Since this process makes use of the adhesive properties of zein, any type of fiber with a hydrophilic surface can be incorporated into the matrix materials.

The developed composites can be used as substitutes for existing commercial products where biodegradation is desirable, such as plant pots, golf tees, clay targets (skeets), lightweight construction material or as a binder for foods and drugs. Recently, it is proposed that the composite can be used as a carrier for the pesticides. As an example, a composite has been fabricated with intoxicated yeast (Fig. 14). Since the matrix material is a living microorganism, the processing pressure needed to be maintained at a much lower value (15 lb/cm^2). Other than that, the fabrication procedure is exactly the same as those of other composites. As the test result with living insects was satisfactory, filing a patent is in progress.

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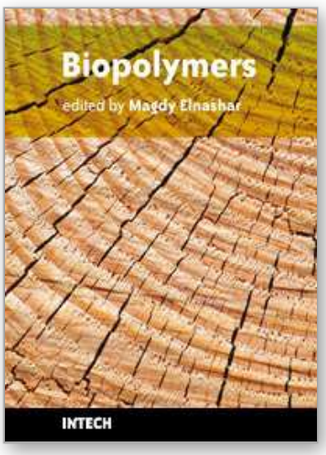

Biopolymers

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Biopolymers are polymers produced by living organisms. Cellulose, starch, chitin, proteins, peptides, DNA and RNA are all examples of biopolymers. This book comprehensively reviews and compiles information on biopolymers in 30 chapters. The book covers occurrence, synthesis, isolation and production, properties and applications, modification, and the relevant analysis methods to reveal the structures and properties of some biopolymers. This book will hopefully be of help to many scientists, physicians, pharmacists, engineers and other experts in a variety of disciplines, both academic and industrial. It may not only support research and development, but be suitable for teaching as well.

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