

# Synthesis of Poly(butylene succinate)/Glass Fiber Composite by Irradiation and Its Biodegradability

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**ABSTRACT:** A composite was synthesized by irradiation of poly(butylene succinate) (PBS) and glass fiber (GF) in the presence of a polyfunctional monomer, trimethylol isocyanurate (TMAIC), which accelerates gel formation of the matrix (PBS) in the composite. The highest gel fraction was achieved at 1% concentration of TMAIC at the dose level of 200 kGy compared to other concentrations. Mechanical properties of the composites were highly dependent on the gel fraction of the polymer and volume fraction of glass fiber reinforcement in the composite. Optimal conditions to syn-

thesize a PBS/GF composite reaching maximum value of bending strength were 1% TMAIC, 67% fiber volume fraction, and irradiation dose of 200 kGy. These synthesized PBS/GF composites can be degraded by enzymes produced from the microorganism population in soil. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2122–2127, 2004

**Key words:** poly(butylene succinate); polyfunctional monomer; composites; crosslinking; biodegradable

## INTRODUCTION

Polymer/fiber composites are finding wider applications in the construction industry. The main features of the composite materials are high fracture energy, ease of fabrication, and potential low cost. To date, glass fiber continues to be the most widely used reinforcement for polymers because of its high strength, low density, and low cost.<sup>1</sup> Epoxy resin, alkyd resin, phenolic resin, polyamide, and silicone, for example, are typical resins used as binder or matrix in composite materials because of their chemical and heat resistance, high strength, and low cost. However, most of these materials are not biodegradable and cause serious environmental problems.<sup>2</sup>

Increasing environmental awareness and decreasing dump space continue to prompt the search for new materials that have recycling and disposal possibilities. Increasing attention has been focused on the research and development of biodegradable polymers.<sup>3,4</sup> Aliphatic polyesters like poly( $\epsilon$ -caprolactone) (PCL) and poly(butylene succinate) (PBS) are among the most promising materials for the production of biodegradable sheets and films. These polymers are converted to carbon dioxide and water when in con-

tact with soil that contains microorganisms; thus they are known as environmentally friendly polymers. PBS, also known by the trade name Bionolle, with high molecular weights ranging from several tens of thousands to several hundreds of thousands, was introduced in 1990 and produced in a pilot plant with a capacity of 3000 tons/year in 1993 by Showa High Polymer Co., Japan.<sup>5</sup> This polymer can be used as a matrix binder in composite materials if its properties are improved.

Radiation is a convenient method used to improve certain properties of polymers such as heat resistance, solvent resistance, and strength by crosslinking. The heat resistance of PCL was improved by radiation crosslinking in the supercooled state.<sup>6</sup> The heat stability of PBS3001 with high molecular weight and smaller peak area of crystal melting has been improved by using a two-step irradiation method attributed to high gel formation.<sup>7</sup>

Radiation crosslinking in the presence of polyfunctional monomers (PFM) (i.e., monomers containing more than one double bond) such as allyl methacrylate (AMA), has been studied for poly(vinyl chloride), cellulose acetate, polymethyl methacrylate, and other polymers. This reaction is of interest because it allows crosslinking to occur at reduced doses compared to those normally required. The presence of polyfunctional monomers such as allyl methacrylate, allyl acrylate, and diallyl maleate has been found to greatly increase the efficiency of polyethylene crosslinking. The results obtained in the studies on polyethylene

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showed that the presence of 4.5% AMA strongly affected the course of the crosslinking reaction at low doses (<3 kGy), but did not change the ultimate effect of the irradiation.<sup>8,9</sup> Polystyrene was also irradiated by gamma rays in the presence of some crosslinkers to achieve a specific degree of crosslinking.<sup>10</sup>

The present article deals with the synthesis of PBS/glass fiber (GF) composites by electron beam irradiation in the presence of a polyfunctional monomer, trimethyllyl isocyanurate (TMAIC). The aim of this work was to investigate crosslinking behavior, strength of composite, and its biodegradability.

## EXPERIMENTAL

### Materials

PBS3001 (molecular weight  $2.96 \times 10^5$ ; melting point of 92°C), produced at Showa High Polymer Co. (Japan), was used. The polymer was dried in a vacuum oven at 50°C for 24 h before use. The solvent used was chloroform (Cica-Reagent, Kanto Chemical Co., Japan). TMAIC was produced by Nippon Kasei Co. (Japan). Glass fiber in mesh with a thickness of 0.09 mm was purchased from Kanebo Co. (Japan).

### Preparation of composites

PBS solution for coating was prepared by dissolving the required amount of PBS in chloroform at 40°C to form a homogeneous solution. The different contents of TMAIC (0, 1, 3, and 5%) were expressed as percentage ratio of monomer to total mass of PBS in solution. Both sides of a glass fiber cloth ( $120 \times 120 \times 0.09$  mm) were coated by the prepared solution using a paint brush. The solution was brushed on the glass fiber cloth as carefully and as uniformly as possible. After that, the coated cloth was dried at ambient temperature for 15 h. The composite samples were fabricated in a hot press machine (Ikeda). Five and 10 pieces of coated glass fiber cloth were used to obtain a laminate sheet of 0.5 or 1.0 mm thickness, respectively. First, five or 10 pieces of glass fiber cloth were coated with PBS solution then preheated at 150°C for 3 min and pressed at the same temperature for another 3 min at a pressure of 50 kg/cm<sup>2</sup>. The sheets were cooled to room temperature by a cold press using water as coolant for 3 min at a pressure of 120 kg/cm<sup>2</sup>.

### Irradiation of the samples

Samples were packaged in poly(vinylidene chloride) bags and sealed using a vacuum machine. Irradiation of samples was carried out by using an accelerator with energy of 2 MeV, beam current of 1 mA, and a dose rate of 10 kGy/pass at a dose range of 0 to 250 kGy.

### Gel fraction

Samples were cut into small pieces and then wrapped with a stainless net. The soluble fraction was extracted by refluxing with chloroform for 48 h. The samples were dried at room temperature after extraction and were kept in a vacuum oven at 50°C to a constant weight. The gel fraction was calculated as follows:

$$\text{Gel fraction (\%)} = (W_g/W_i) \times 100 \quad (1)$$

where  $W_g$  is the weight of gel and  $W_i$  is the initial weight of PBS.

### Mechanical properties

Bending strength and modulus of samples were measured in a Stograph-R1 Material Tester (Toyoseiki Co., Japan) and an Instron 4302 (Instron, Canton, MA), at a crosshead speed of 10 mm/min and beam of 25 mm. Samples were cut into dumbbell-shape pieces to measure tensile strength and elongation at break at a crosshead speed of 50 mm/min and beam speed of 25 mm/min according to ASTM D-1822-L.

Dynamic viscoelastic properties were measured by using a torsion pendulum-type viscoelastometer (Rhesca RD-1000AD; SHESCA Co. Ltd., Japan) at 0.2 to 1.0 Hz in the temperature range of -150 to 100°C. Measurements were carried out by heating from -150°C at a rate of 1°C min<sup>-1</sup>. Sample sizes of  $100 \times 10 \times 0.5$  mm were used.

### Biodegradation test

The biodegradation tests were carried out by determining the weight loss of samples (irradiated and unirradiated) fabricated from chosen conditions after soil burial.

The soil burial test was carried out in plastic troughs, containing half rusty soil and half black garden soil. The pieces were buried about 3 cm below the soil surface so that the oxygen supply was sufficient and kept for different burial times from 2 weeks to 4 months. This experiment was carried out from April to August in Takasaki, Japan. The samples were removed from the soil, cleaned using running water, and dried in a vacuum oven to a constant weight at 50°C. The weight loss of the samples after the soil burial test was calculated using the following equation:

$$\text{Weight loss (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \quad (2)$$

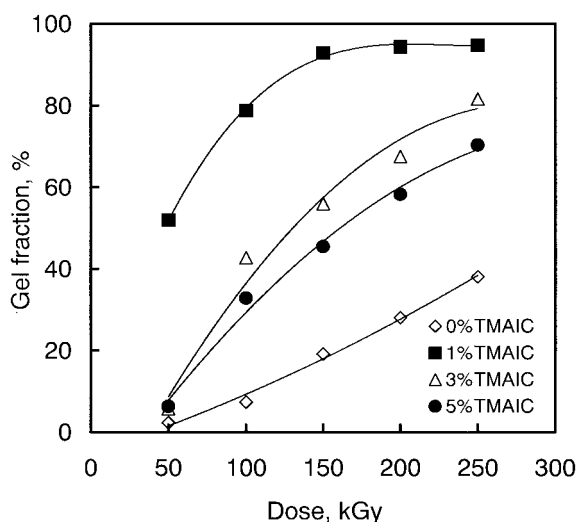
where  $W_0$  and  $W_1$  are the weight of PBS in PBS/GF composite before and after the soil burial process, respectively.

## RESULTS AND DISCUSSION

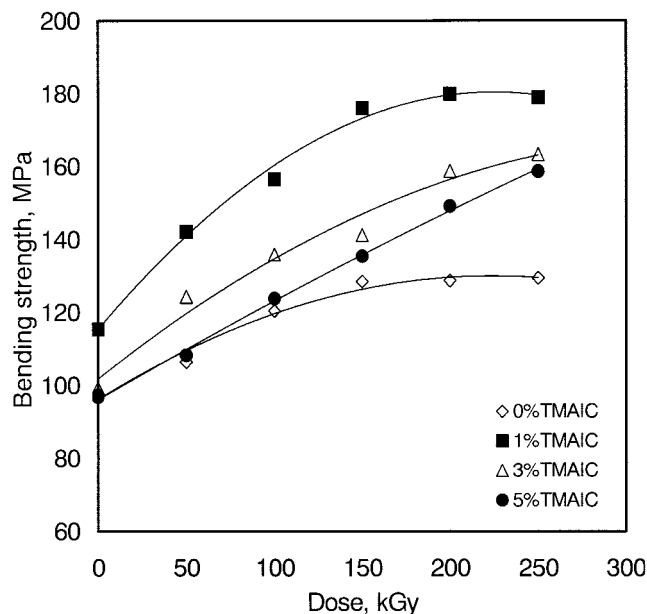
### Gel fraction of PBS/GF/TMAIC composite

Crosslinking and chain scission are among the chemical effects observed when polymers are subjected to ionizing radiation. Crosslinking or degradation may occur depending mainly on their chemical properties and irradiation conditions.<sup>11–13</sup> The processes ultimately cause formation of insoluble gel if crosslinking predominates over scission. Figure 1 shows the effect of different contents of TMAIC on the crosslinking of PBS at various irradiation doses. PBS3001 is a crosslinkable polymer, as evidenced by the formation of gel in the absence of crosslinking agent, when exposed to electron beams under vacuum, but to a low degree. In the presence of TMAIC, the crosslinking degree is expressed more clearly. The gel fraction increases with increasing irradiation dose. The highest value of gel fraction in samples containing 1% TMAIC reached 94% at a dose of 200 kGy. Content of TMAIC higher than 1% did not show a further increase of gel fraction. Gelation doses, calculated according to the Charlesby–Rosiak equation, were 51.1, 28.8, 44.95, and 41.35 kGy for samples containing 0, 1, 3, and 5% TMAIC, respectively. Thus, in this case, a suitable content of TMAIC as a crosslinking agent and an effective irradiated dose were found.

The crosslinking of polymers is formed by the recombination reaction of radicals during irradiation. The reactions occur predominantly in the amorphous region because of the high mobility of the molecular chains. The monomer-crosslinking reaction would be expected to occur only in the amorphous region of polymer because the monomer would be present only in those regions.<sup>8</sup> PBS3001 has low crystallinity and melting point, and a small area of crystal melting ( $\Delta H$



**Figure 1** Gel fraction of PBS/GF sample with different TMAIC concentrations as a function of dose.

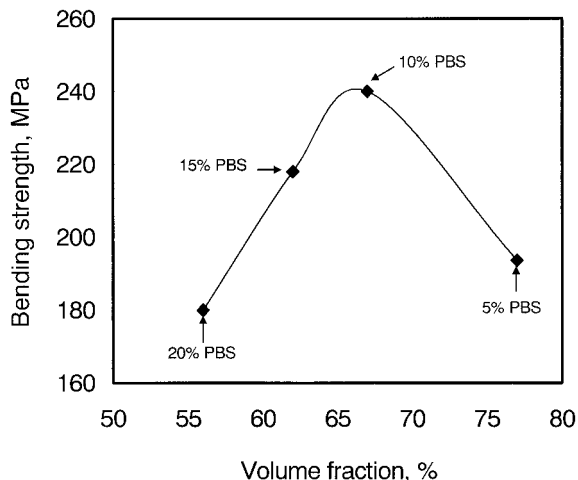


**Figure 2** Bending strength of PBS/GF sample with different TMAIC concentrations as a function of dose. Thickness of 1.0 mm.

= 45 J/g). The gel content was around 28% at a dose level of 200 kGy in the TMAIC-free samples. Similar results were also obtained with the same material by gamma irradiation but at a dose of 160 kGy.<sup>7</sup> Moreover, in the presence of TMAIC, free radicals are produced by irradiation from breaking of double bonds in methallyl groups in its chemical structure. These radicals play an important role in linking polymer chains and forming three-dimensional networks.

### Effect of gel content on mechanical properties

Gel formed by radiation crosslinking has an effect on the mechanical, physical, and chemical properties of polymers and causes changes to the quality of the original materials. The formation of PBS gels in the matrix influences the strength of the composite. Figure 2 shows the bending strength of PBS/GF composites as a function of irradiation dose. Bending strength of composites increases with respect to the formation of gel at doses up to 250 kGy. The irradiated sample, containing 1% TMAIC at the dose of 200 kGy, achieved the highest bending strength value, which was 1.56 times higher than that of the unirradiated sample. This value corresponds to the highest value of gel fraction obtained. The other measured values of bending strength were about 158 and 149 MPa at the dose of 200 kGy for samples containing 3 and 5% TMAIC, respectively, and were lower than those of samples containing 1% TMAIC. From the experimental results it can be deduced that bending strength of



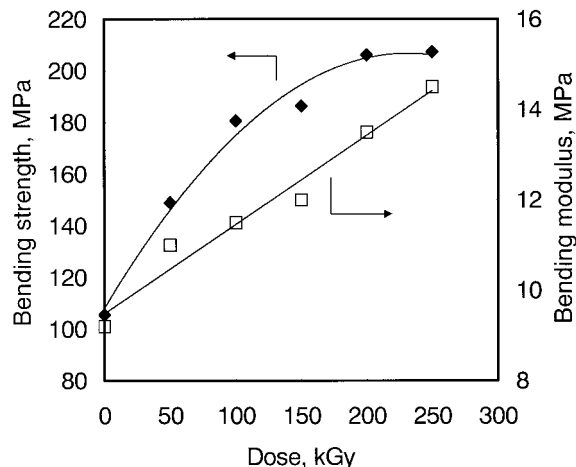
**Figure 3** Relationship between bending strength and fiber volume fraction. Irradiated at dose of 200 kGy. Thickness of 1.0 mm.

these composite materials depends substantially on gel fraction.

**Effect of glass fiber volume fraction on mechanical properties**

The mechanical/physical properties of composite materials are controlled by the constituents of their components. The strength and stiffness of complex engineering materials depend on the properties of the reinforcing agent, the matrix, and their interface. Each of these individual phases has to perform certain essential functional requirements based on their mechanical properties so that a system containing them may perform satisfactorily as a composite. There are many factors that influence mechanical properties of composite such as the fiber volume fraction of the composite, the mechanical properties of the fiber and matrix, and the strength of the fiber–matrix bond.<sup>1</sup> In this study, the suitable volume fraction of glass fiber was estimated.<sup>14</sup> Glass fabrics were coated with different concentrations of PBS solution (5, 10, 15, and 20%). These concentrations were expressed as percentage ratio of PBS in chloroform solvent (w/v). PBS/GF/1%TMAIC composites were irradiated at the same dose of 200 kGy. Figure 3 shows the relationship between fiber volume fraction ( $V_f$ ) and bending strength. The strength of the composite depends on fiber content in its constituents. The highest value was measured in samples containing a  $V_f$  of 67%. At the lower and higher values of  $V_f$ , only lower values of bending strength were obtained. Thus, 10% PBS solution is suitable for coating on fiber cloth to laminate a composite.

Figures 4 and 5 show bending strength and modulus of these composites with 67% volume fraction as a

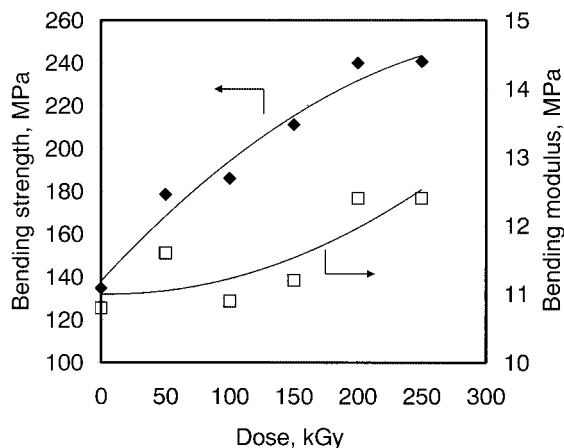


**Figure 4** Bending strength and modulus of PBS/GF/1%TMAIC sample as a function of dose. Thickness of 0.5 mm.

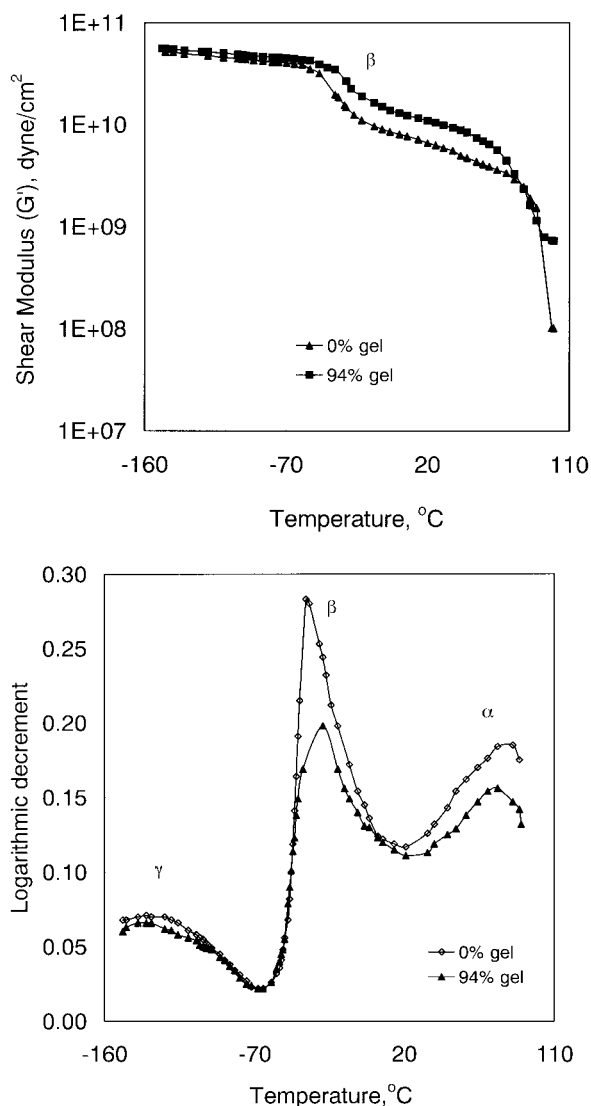
function of irradiation dose. For both thicknesses, bending strength and modulus values increase with increase of dose. Samples of 0.5 mm thickness (Fig. 4) gave higher bending strength of 1.95 times and bending modulus of 1.46 times at a dose of 200 kGy compared to those of unirradiated samples. In samples of 1.0 mm thickness (Fig. 5), a bending strength of 1.79 and modulus of 1.15 times were measured. The results show that the thickness of samples caused an enhancement in bending strength and a reduction in bending modulus. All of the above-mentioned results confirm that a composite can be prepared from optimal conditions (1%TMAIC, 67%  $V_f$  and irradiation dose of 200 kGy).

**Dynamic mechanical properties**

The changes in mechanical properties are induced mainly by chain scission and/or crosslinking. The ra-



**Figure 5** Bending strength and modulus of PBS/GF/1%TMAIC sample as a function of dose. Thickness of 1.0 mm.



**Figure 6** (a) Temperature dependency of shear modulus for uncrosslinked and crosslinked PBS/GF samples. (b) Temperature dependency of mechanical loss for uncrosslinked and crosslinked PBS/GF samples.

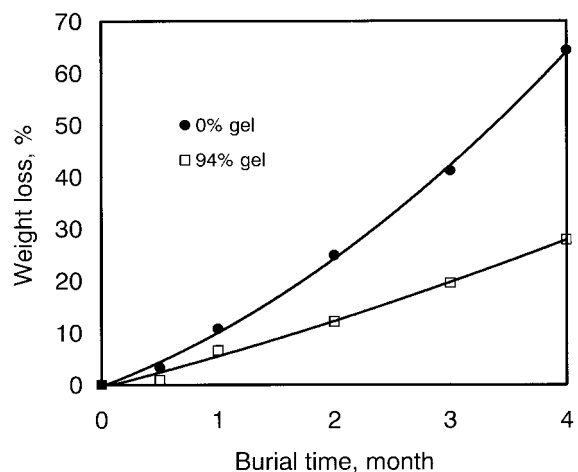
diation-induced chemical reactions are evaluated by the levels of gel fraction, and information about chain scission and/or crosslinking can be elucidated from the measurements of the molecular motions.<sup>15</sup>

The difference in degradation mechanism between uncrosslinked and crosslinked PBS in PBS/GF composites was investigated. All of the samples used in this study showed two distinct relations. Figure 6(a) shows the temperature dependency of shear modulus ( $G'$ ) of irradiated PBS with 94% gel and the nonirradiated sample with 0% gel. At a temperature below the  $\beta$ -relaxation, the shear moduli of uncrosslinked and crosslinked samples were insignificantly different. The shear modulus decreases sharply at the  $\beta$ -relaxation temperature: the  $\beta$ -relaxation can be attributed to the molecular motion of chains during the

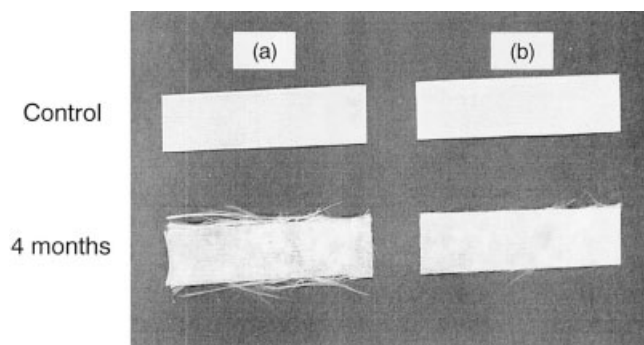
glass transition.<sup>16</sup> Furthermore, the glass transition shifts to higher temperature and the modulus above the glass-transition temperature ( $T_g$ ) increases with the crosslinked sample. It can be concluded that crosslinking density is increased by electron beam irradiation at a dose of 200 kGy in the presence of 1% TMAIC. Figure 6(b) shows the temperature dependency of the mechanical loss of nonirradiated and irradiated samples with 0 and 94% gel, respectively. No substantial difference was observed in the  $\gamma$ -relaxation region (local motion). The  $\beta$ -relaxation, appearing in the highest temperature region, can be attributed to the three-dimensional motion of chains between crosslinking points, given that the shear modulus decreases sharply at the same time. The  $T_g$  of the 0% gel sample was  $-39^\circ\text{C}$ , whereas the  $T_g$  of the 94% gel sample shifted to  $-29^\circ\text{C}$ . When the crosslink density is increased, molecular motion becomes more restricted, and the  $T_g$  of the crosslinked polymer increases.<sup>17</sup> Moreover, this phenomenon confirmed that the crosslinked sample is more heat stable than the uncrosslinked sample.

#### Biodegradability of the composite

Soil burial is a traditional way to test samples for degradation because of its similarity to actual conditions of waste disposal. This method will be more effective, compared to an enzymatic test, if the samples are buried in suitable climatic conditions and the various populations of microorganisms that are involved. Moreover, several factors such as temperature, pH, humidity, and oxygen availability also may affect the results. Soil burial degradation is expressed as the percentage of weight loss of polymer. Figure 7 shows the relationship between the weight loss of samples and burial time. It is seen that, in cases of



**Figure 7** Weight loss of uncrosslinked and crosslinked samples in soil burial test. Thickness of 0.5 mm.



**Figure 8** Photograph of PBS/glass fiber samples after burial in soil. Thickness of 0.5 mm. (a) 0% gel, (b) 94% gel.

uncrosslinked and crosslinked composites, the weight loss of PBS gradually increases with increasing burial time. After a 4-month burial period, weight loss of 64.3% PBS was achieved in the uncrosslinked composite (0% gel), whereas for the crosslinked composite (94% gel), weight loss was 27.9%. From this result, it is assumed that the weather at Takasaki from April to August is suitable for carrying out a burial test. The weight loss of unirradiated composites is higher than that of the irradiated composites. This is attributed to crosslinking in the network structure of irradiated samples expressed through formation of gel. A photograph of PBS/glass fiber-reinforced composites, after burial in soil for different periods, is shown in Figure 8. It is apparent that these composites were eroded by the presence of microorganisms in the soil. The microorganisms use the PBS matrix as their food source. In this photograph, degradation of PBS in the composite was seen clearly, after the 4-month period, by the exposure of glass fiber.

### CONCLUSIONS

A new composite based on biodegradable polymer/glass fiber was synthesized by electron beam irradiation in the presence of TMAIC as a crosslinking agent. The composite strength strongly depends on the gel fraction of the matrix (PBS) and the volume fraction of filler (glass fiber) in the composite. Crosslinked

PBS/GF composite can be degraded by enzymes produced from microorganisms in soil. In this way, glass fiber can be recovered after composite degradation and recycled for other purposes, which would be useful for reduction of environmental pollution.

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