# THE HEAT STABILITY OF RADIATION CROSSLINKED OF BIONOLLE

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## ABSTRACT

**THE HEAT STABILITY OF RADIATION CROSSLINKED OF BIONOLLE.** Bionolle with chemical names Poly (butylene succinate-co-adipate), Poly(butylene succinate) (PBS), were irradiated using electron beam (EB) in the presence of five different polyfunctional monomers at ambient temperature. It was pointed out that the highest amount of gel fraction could be achieved when PBS was blend with trimethallyl isocyanurate (TMAIC). It was obtained that crosslinked PBS containing 1% of TMAIC produces higher gel fraction than that crosslinked PBS containing 2 or 3% of TMAIC at dose of 50 kGy. The PBS containing 1% of TMAIC also has higher glass transition ($T_g$) than that of original PBS. It was observed that the presence of crosslinking bonds in irradiated PBS greatly improved its heat stability as well as diminished its ability to biodegradation. Accordingly, it can be concluded that crosslinked PBS in the presence of TMAIC has significantly improved heat resistant properties.

***Key words*** : Poly(butylene succinate)(PPS), electron beam irradiation, trimethallyl isocyanurate (TMAIC), heat stabilitas.

## ABSTRAK

**KESTABILAN PANAS DARI RADIASI PENGIKATAN SILANG BIONOLE.** Bionole dengan nama kimia Poli(butilen suksinat-co-adipat), Poli(butilen suksinat) (PBS), di iradiasi menggunakan berkas elektron pada suhu ruangan dengan penambahan polifungsional monomer sebagai aditif. Dari lima jenis polifungsional monomer yang dipergunakan diperoleh bahwa hasil kandungan gel tertinggi diperoleh bila PBS di campur dengan trimetalil isosianurat (TMAIC). Jumlah TMAIC yang ditambahkan sangat berpengaruh pada jumlah gel yang dihasilkan. Diperoleh bahwa PBS iradiasi yang mengandung 1% TMAIC menghasilkan kandungan gel lebih tinggi dibandingkan dengan PBS iradiasi yang mengandung 2% atau 3% TMAIC pada dosis iradiasi 50 kGy. PBS iradiasi yang mengandung 1% TMAIC mempunyai suhu transisi glas ($T_g$) yang lebih tinggi dibandingkan PBS asal. Diperoleh bahwa ikatan silang yang terjadi meningkatkan kestabilan panasnya, sebaliknya juga mengurangi kemampuan PBS untuk terdegradasi. Dari percobaan ini dapat disimpulkan bahwa TMAIC sebagai aditif pada iradiasi PBS secara nyata meningkatkan kestabilan panas dari contoh.

***Kata kunci :*** Poli(butilen suksinat) (PBS), iradiasi berkas elektron, trimetalil isosianurat (TMAIC), kestabilan panas

## INTRODUCTION

In the past decade, as an active response to environmental concerns about the disposal of non degradable municipal and industrial plastic waste. Showa high polymer Co. Ltd developed high molecular weight (ranging from several tens of thousands to several hundreds of thousands) commercial aliphatic PBS and a series of its copolyesters like poly(butylene succinate-co- adipate) with the commercial name of Bionolle. Bionolle is considered to be the most economically competitive of the biodegradable polymers[1]. It is utilized in farming as plant covers and releasing fertilizer, also is utilized for plastic bag, net rope and for medical utilization. However, the insufficient thermal properties of these polymers prevent them from being used in a variety of targeted applications. Blending and copolymerization techniques have been tried to obtain biodegradable polymers with improved properties[2].

Irradiation processing in supercooled state can improve heat resistance and process ability of Poly(e-caprolactone) (PCL)[3]. Poly(butylene succinate) PBS has been studied to produce a biodegradable foam by electron beams irradiation[4]. It was known that useful products of polymer could be produced only if certain additives were incorporated into polymer. With the help of suitable additives, the heat stability, mechanical properties and process ability of plastic can be improved. A specific monomer distribution in the polymer chains of aliphatic polyesters formed good material properties with a reasonable price level and biodegradability[5,6]. It was observed that the physical properties of aliphatic polyesters were improved as a result of addition of aromatic units into the polymer[7,8].

Radiation crosslinking is major technology of radiation processing in the industry. PBS has melting temperature in the range of 90~120°C, its thermal properties are similar to that of polyethylene. PBS has deformation by contacting of hot water. Thus, improvement of heat resistance of this polymer is essential for expansion of its application field. The well-known method to achieve such improvement of polymer properties is to crosslink new composition by use of ionizing radiation. In this study, radiation crosslinking behaviors of PBS in the presence of polyfunctional monomer and its properties were investigated.

## EXPERIMENTAL

### Materials

Some properties of Bionolle samples used in this study are shown in Table 1. These polymers were produced at Showa High Polymer Co. Ltd., Japan.

To prepare the mixed materials, some polyfunctional monomers (PFM) were used. The structures of polyfunctional monomers are shown in Table 2.

### Preparation of Samples and Irradiation

The content of monomer in final compositions were expressed as percent ratio of monomer to total mass of samples, PBS and additives were mixed in a labo plastomill model 50C150 (Toyo Seiki). The speed of mixing was 20 rpm, at 150°C. Each sample was pressed to form 0.5 mm thickness sheet in an Ikeda hot press at 150°C, samples were preheated for 3 min then were heated at the same temperature for another 3 min at pressure of 120 kgf/cm², then cooled to room temperature by cold press using water as a coolant for 3 min. Irradiation of samples was carried out in plastic bag using an accelerator with energy of 2 MeV and current of 1 mA, at various doses from 10 to 100 kGy at a dose rate of 10 kGy/pass.

### Gel Fraction Measurement

Gel content in irradiated samples was estimated after removing of the soluble part by extraction in boiling chloroform for 48 h. The gel fractions were calculated as a ratio of weight of dried gel to the initial weight of the polymer.

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

where $W_g$ is the weight of gel and $W_i$ is the weight of original sample.

### Analytical Measurement

Thermomechanical analyzer (Shimadzu TMA-50) was used to evaluate the heat stability. The thin PBS films with a dimension of 5 x 2 x 0.1 mm was put into sample holder and heated under nitrogen atmosphere from 25°C to 200°C, under constant load of 0.5 g with a heating rate of 10°C/min.

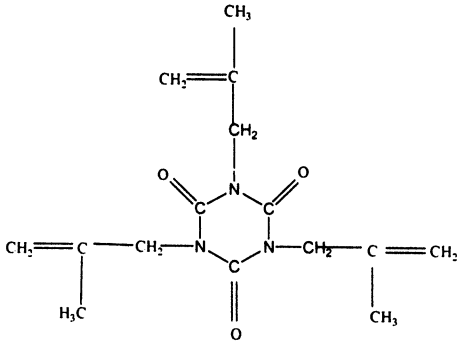
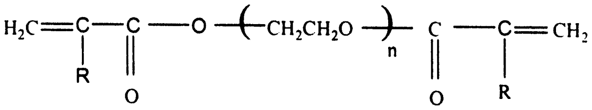
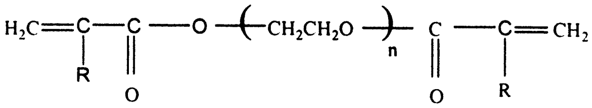
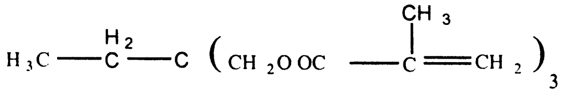
Heat resistance of sample was investigated by creep test using a burner. The PBS sheets with a dimension of sample 0.5 x 10 x 50 mm was hanged out with applied stress of 0.23 MPa, the deformation of sample (in elongation) was measured at different temperature for 3 minutes then the applied stress of 0.21 MPa was removed to estimate the rearrangement of sample.

Dynamic viscoelastic properties were measured by using a torsion –pendulum-type viscoelastometer (Rhesca RD-1000AD) at 0.2 to 1 Hz in the temperature range of –150 to 150°C. Film samples 100 X 10 mm² and 0.5 mm thick were used.

***Table 1.*** Some properties of Bionolle samples used in this work.

| Sample type | Mw | Mw/Mn | Melting point (°C) | Density (g/cm³) | ΔH (J/g) |
|---|---|---|---|---|---|
| PBS1 (Bionolle#3001) (Poly(butylene succinate-*co*-adipate)) | $2.96 \times 10^5$ | 2.0 | 92 | 1.23 | 45 |
| PBS2 (Bionolle#3002) (Poly(butylene succinate-*co*-adipate)) | $1.56 \times 10^5$ | 1.62 | 93 | 1.23 | 44 |
| PBS3 (Bionolle#1001) (Poly(butylene succinate)) | $1.75 \times 10^5$ | 1.8 | 114 | 1.26 | 72 |

***Tabel 2.*** Structure of polyfunctional monomer used in this work

| Name | Structure | Mw |
|---|---|---|
| Trimethallyl isocyanurate<br>(TMAIC) |  | 291 |
| Polyethyleneglycol dimethyl methacrylate (2G) |  $H_2C{=}C(R)-C(=O)-O-(CH_2CH_2O)_n-C(=O)-C(R){=}CH_2$ | 242 (2G) |
| Polyethyleneglycol dimethyl methacrylate (4G) |  $H_2C{=}C(R)-C(=O)-O-(CH_2CH_2O)_n-C(=O)-C(R){=}CH_2$ | 330 (4G) |
| Trimethylolpropane trimethacrylate<br>(TMPT) |  $H_3C-CH_2-C(CH_2OOC-C(CH_3){=}CH_2)_3$ | 338 |
| Trimethylolmethane tetraacrylate<br>(A-TMMT) | $C(CH_2OOC-HC{=}CH_2)_4$ | 352 |

## RESULTS AND DISCUSSION

### Crosslinking Behaviors of Irradiated PBS

Poly(butylene succinate) (PBS) is known as a crosslinkable polymer. When the polymer is exposed to electron beams from accelerator the molecular weight of the polymer increases and forms an insoluble fraction, called a gel fraction. This process affects mechanical, physical, and chemical properties of polymer and changes the quality of the original material.

The gel content of PBS1 in the presence of 1% weight of different monomers against dose of irradiation is shown in Figure 1. The gel fraction of irradiated pure PBS1 is equal to 18.23% at irradiation dose of 50 kGy. For mixed samples, the gel content increases significantly. At irradiation dose of 50 kGy, PBS1 with high gel fraction (82.9%) was produced by adding of TMAIC, the gel fraction was constant up to the end of experiment dose at irradiation dose of 100 kGy. Whereas the gel content of irradiated PBS1 containing A-TMMT and TMPT respectively was lower than that of irradiated PBS1 containing TMAIC. Addition of 2G and 4G displayed a low effect on the yield of gel formation of irradiated PBS1. Obviously, TMAIC gave higher gel content in radiation crosslinking of PBS1 in comparison with the other monomers. TMAIC has additional allylic hydrogens as a-methyl group in which no steric hindrance may occur for the transition state formation of monomer chain transfer reaction. The formation of

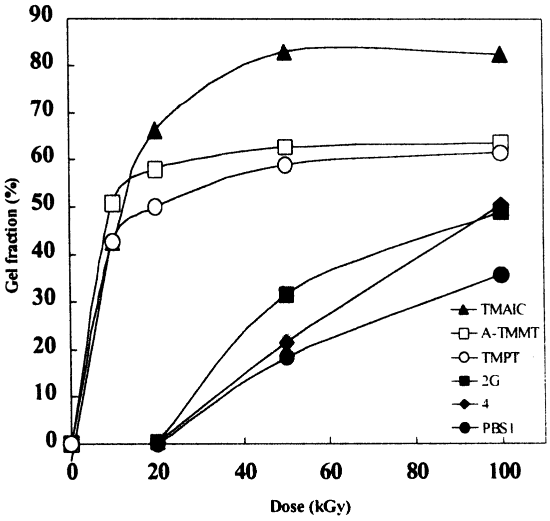


***Figure 1.*** Gel fraction-dose curves for PBS1 1% weight of different kind monomers (TMAIC, $3.44 \times 10^{-3}$ mol%; A-TMMT, $2.84 \times 10^{-3}$ mol%; TMPT, $2.96 \times 10^{-3}$ mol%; 2G, $4.13 \times 10^{-3}$ mol%; 4G, $3.03 \times 10^{-3}$ mol%)

monomer chain transfer reaction occurred by the abstraction of allylic hydrogens of a-methyl group, which are located at the d-site from the isocyanuric[9]. Also TMAIC has cyclic unit that achievable more three-dimensional network by irradiation than that of aliphatic polyfunctional monomers. It is well known when the bulk polymers are irradiated, the dominant reactions and the final products depend strongly on the transport of excitation energy (and charge), strengths of individual chemical bonds, and on the geometrical arrangements of the polymer molecules. Usually, one of the two general processes dominates: cross-linking or degradation[10].

Figure 2., shows the gel contents of irradiated PBS1 with different concentrations of TMAIC. It can be seen that at irradiation doses of 10 kGy and 20 kGy sample with 0.2%, 0.5%, and 1% amount of TMAIC form higher gel content than that of sample contains 2% and 3%. Where as at irradiation dose of 100kGy addition of 2% and 3% TMAIC formed higher gel content than that of 0.2%, 0.5% and 1%. These results probably because at irradiation dose of 10 kGy and 20 kGy, the PBS1 containing 2% and 3% TMAIC formed insufficient radicals (only one side) in TMAIC to react for supporting crosslinking network between polymer. Therefore the monomer reacted only with one layer side of polymer. While PBS1 which contain 2% and 3% TMAIC at irradiation dose of 100 kGy, resulted sufficiently radicals in TMAIC to react with polymer during irradiation, at this condition all monomer reacted with polymer to form three dimensional network in polymer.

The yield of gel formation of PBS1 containing 0.2%; 0.5% and 1% TMAIC at irradiation dose of 50 kGy insignificantly different from that of irradiation dose of 100 kGy. It is due to the fact that all of the monomer had been used to form crosslinking when the sample was irradiated at 50 kGy.

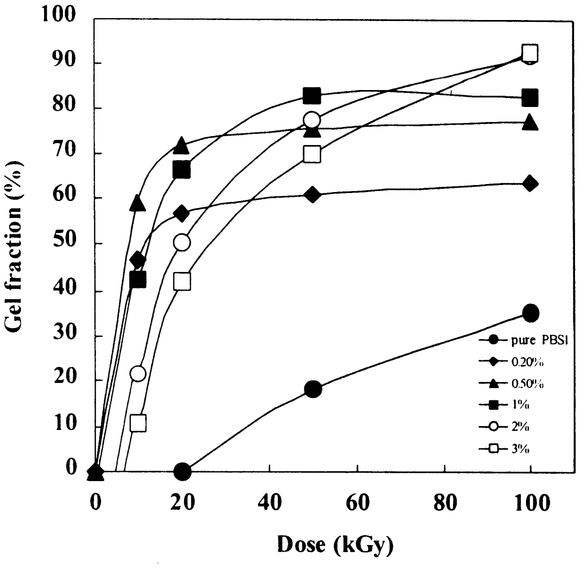


***Figure 2.*** Gel fraction-dose curves for PBS1 with TMAIC in different concentrations.

Figure 3., shows the gel contents of irradiated PBS2 with different concentrations of TMAIC, it can be seen that TMAIC obviously, enhanced the yield of gel formation of irradiated PBS2. At dose of 10 and 20 kGy, PBS2 containing 0.5% and 1% TMAIC result higher gel content than that of PBS2 containing 3% TMAIC. On the contrary, at dose of 100 kGy addition of 3% of TMAIC gave higher gel content than that of 0.5% and 1%. These phenomena are same as that of irradiated PBS1 containing TMAIC as mentioned above and also similar behaviors were pointed out for PBS3 (Figure 4).

The effect of TMAIC concentration in the irradiated PBS1 (irradiation dose of 50 kGy) is shown in Figure 5. One can see that irradiated PBS samples containing 1% TMAIC have highest gel fraction. This is

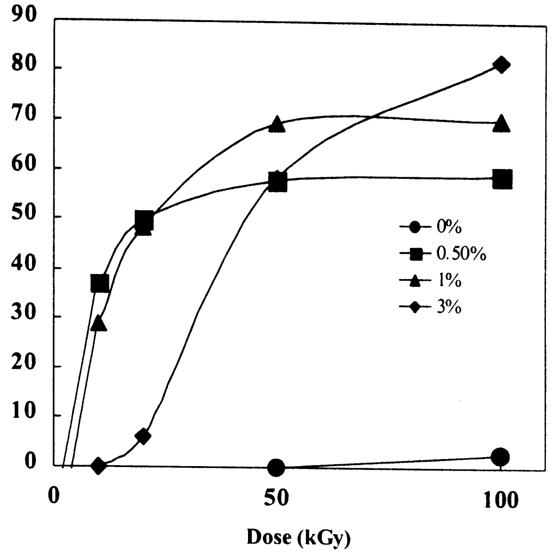


***Figure 3.*** Gel fraction-dose curves for PBS2 with TMAIC in different concentrations.

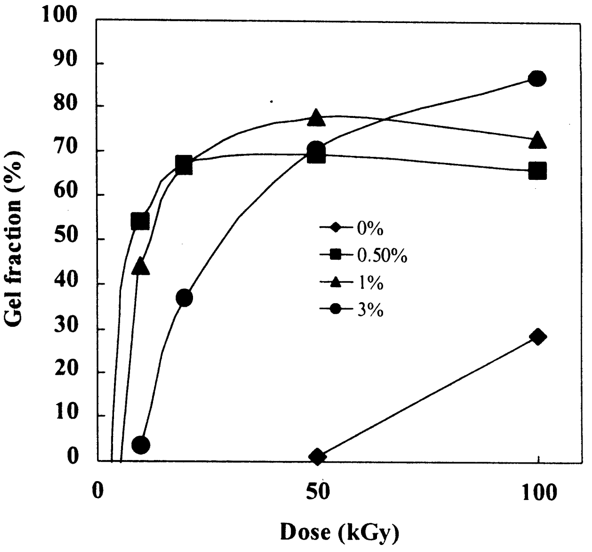


***Figure 4.*** Gel fraction-dose curves for PBS3 with TMAIC in different concentrations.

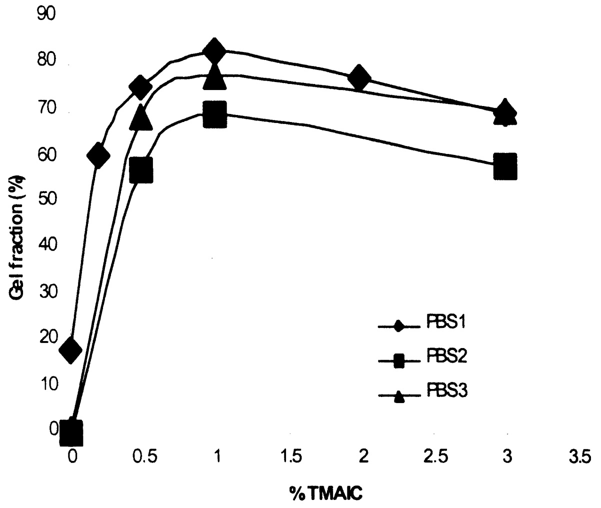


*Figure 5.* Gel fraction-TMAIC concentrations curves for irradiated PBS at irradiation dose of 50 kGy.

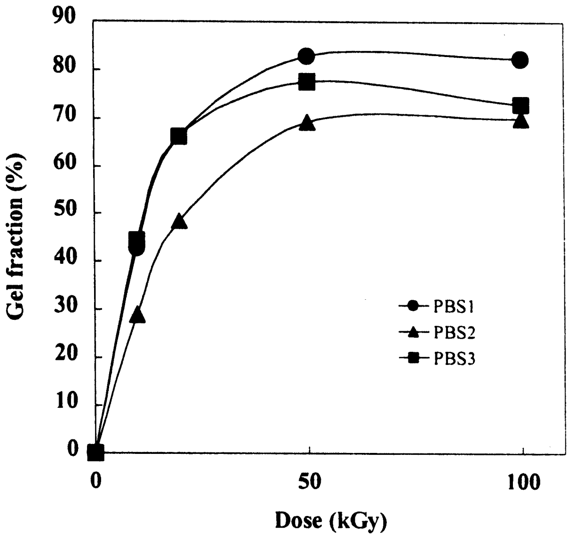


*Figure 6.* Gel fraction of PBS contains 1% of TMAIC

due to at this condition (50kGy irradiation dose; 1% TMAIC), the polymer radicals have optimum amount to react with TMAIC radicals.

Figure 6., shows that irradiated PBS1 formed higher yield of gel formation in the presence of TMAIC compare to those of PBS2 and PBS3. It can be explained that the crosslinking of polymers is due to formation of intermolecular bonds. It is known that the phenomenon is remarkably affected by crystallinity of the polymeric material. The recombination reactions occur during irradiation predominantly in the amorphous regions of the sample. It is probably because of higher mobility of the molecular chains in the amorphous part. PBS1 has higher molecular weight (Mw; 2.96x10$^5$) and lower melting point compare to PBS2 and PBS3, as shown in Table 1. Irradiated PBS1 therefore exhibits higher crosslinking than that of PBS2 and PBS3.

## Heat Stability of Crosslinked PBS1

### Creep Test

Heat resistance of irradiated PBS was determined by measuring the deformation of PBS samples at different temperature beyond the melting point. The applied stress of 0.23 MPa was calculated from the load divided by the cross-sectional area of the sample. The relationship between time and deformation (in

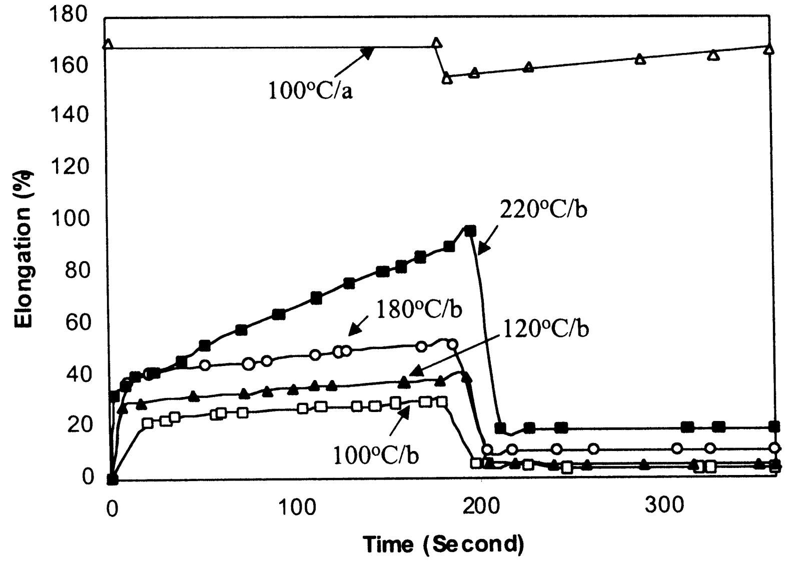


*Figure 7.* Creep test of irradiated PBS1 at irradiation dose of 50 kGy. a:PBS1; b: PBS1 contains 1% of TMAIC

elongation) of irradiated PBS1 with and without TMAIC are shown in Figure 7. It Shows that at 100°C the irradiated pure PBS1 (Irradiation dose of 50 kGy) significantly has higher deformation in elongation compared to that irradiated PBS1 containing 1% TMAIC.

The irradiated pure PBS1 was immediately broken at temperature 120°C while PBS1, which contains TMAIC slightly elongated then recovered after removing 0.21 MPa of applied stress. The recovery of sample is probably due to rearrangement of crystalline part in the sample. Further increase in temperature led to increase of deformation in elongation. Irradiated PBS1 containing 1% TMAIC did not break at 220°C up to the end of experiment's keeping time (6 minutes).

## Dynamic Viscoelastic Properties

The difference in deterioration mechanism between uncrosslinked and crosslinked PBS1 sample was investigated. Crosslinking effects on molecular motions revealed by viscoelastic measurements of semicrystalline PBS1 polymer samples are discussed. Figure 8., shows the temperature dependence of shear modulus (G') of irradiated PBS1 sample contains 1% of TMAIC (83% gel) and pure sample. At temperatures below the *b* relaxation, the shear moduli of uncrosslink and crosslinked sample are insignificantly different. Whereas at *b* relaxation the crosslinked sample shift to higher temperature compare to uncrosslink sample. The decrement in shear modulus in the *b* relaxation region is scarcely affected by the degree of crosslinking in sample. It was obtained that the temperature of onset of fall of crosslinked sample in shear modulus occurring slightly lower than that of pure sample due to decreasing of melting point.

Figure 9., shows temperature dependence of mechanical loss (logarithmic decrement) of crosslinked sample (83% gel) and uncrosslink sample. Two discrete mechanical loss peaks, g and b relaxation are observed. The g relaxation of polymers such as polyethylene, poly(methyl methacrylate) and polystyrene has been attributed to molecular motions of short branching or local motion of chains existing on crystallite surface, or both. For rigid aromatic polymers, the low temperature mechanical relaxation has been attributed to local motion of aromatic units in the main chain.[11,12,13] The g relaxation peak of crosslinked sample broadens could be also assigned to the local motion of cyclic units in the main chain, and the *b* relaxation shifts to higher temperature due to increasing of glass transition. It is known in highly crosslinked materials that the glass transition temperature and the modulus at the rubbery plateau are related to the crosslink density.[14] The glass transition shifts to higher temperature and the modulus increases with increasing of crosslink density.

Increasing glass transition indicates an improving heat stability caused by the need for more heat to support the molecule motion of the sample. These facts demonstrate that the thermal resistance of PBS1 sample is greatly improved by irradiation in the presence of 1% of TMAIC inside PBS1 sample.

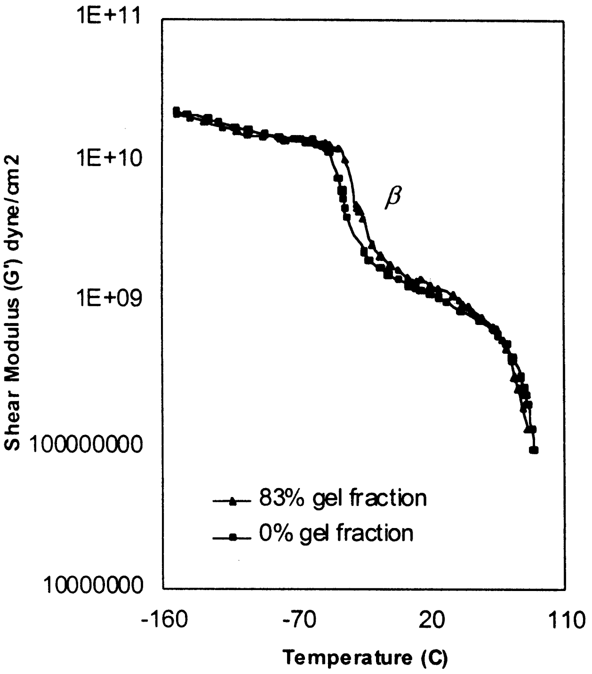


*Figure 8.* Temperature dependence of shear modulus of PBS1 sample.

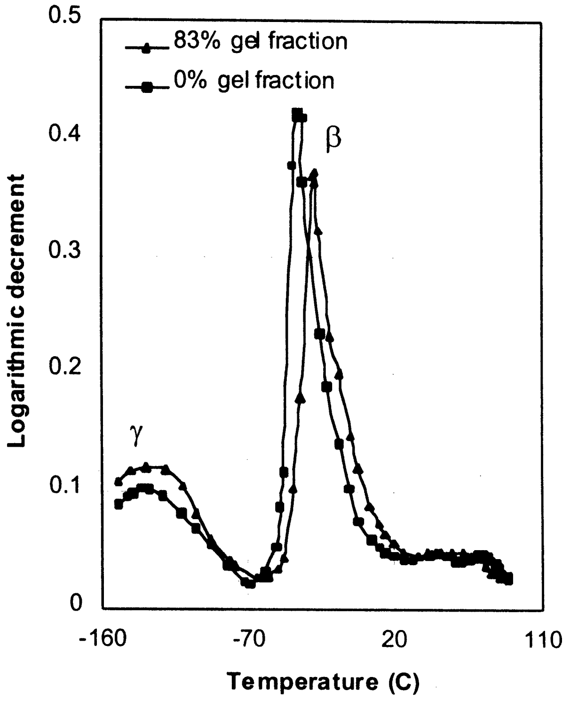


*Figure 9.* Temperature dependence of mechanical logg of PBS1 sample.

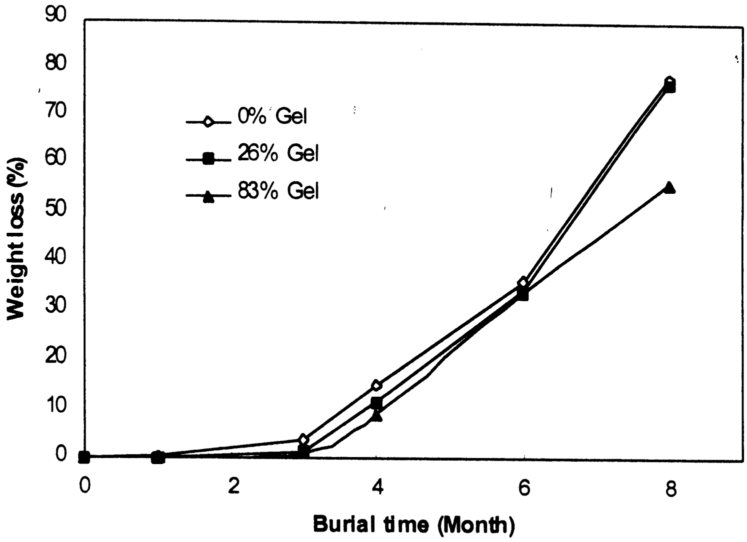


***Figure 10.*** Weight loss of PBS1 in soil burial degradation test.

## Biodegradation Test of Crosslinked PBS

Soil burial test is a standard examination of biodegradability of polymer samples by bacteria in soil. Effect of gel content on biodegradability is shown in Figure 10. It can be seen that weight loss of sample strongly was affected by gel content in the sample. This behavior is similar with the enzymatic degradation (see above). There are several important factors, however, which may affect results of the soil burial test, e.g., temperature, humidity, pH, oxygen concentration, insufficient number of active microorganism, availability of mineral nutrient, etc. To evaluate their effect is a complex task, which needs to follow a set of the parameters in co-ordinance. It was not performed in this work.

## CONCLUSION

Radiation crosslinking of three kind of poly(butylene succinate) (PBS) with different molecular weights in the presence of five kind of polyfunctional monomers respectively, were investigated. It was pointed out that trimethallyl isocyanurate, TMAIC stronger enhanced formations of gel in the irradiated PBS compared to the other polyfunctional monomers. The amount of TMAIC blended with PBS influences the amount of gel resulting after irradiation. Crosslinking took place most efficiently for PBS which contains 1% TMAIC at irradiation dose of 50 kGy. It was obtained that crosslinked PBS1 containing 1% TMAIC has 10°C higher glass transition ($T_g$) than that of original sample. The crosslinked PBS in the presence of TMAIC exhibits largely improved heat stability. The biodegradation rate of modified polymers is slightly diminished with increasing of gel fraction, however, the polymers are still biodegradable.

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