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The Effect of Electron Beam Radiation on Mechanical Stability of Polybutylene Succinate Polymer

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This paper examines the effect of electron beam (EB) radiation on mechanical stability of polybutylene succinate (PBS) blends with three types of cross linking agent has been studied using tensile, flexural, impact, gel content, melt flow index (MFI) and heat deflection temperature (HDT). PBS was radiated using a 3.0MeV electron beam machine with doses ranging from 0 to 120 kGy/ 10 kGy per pass. The results show that 20 kGy depict the most stable mechanical properties. Higher radiation figures higher crosslink density but depicts reduction in most of mechanical properties. Blends with crosslinker such as Triallyl Isocyanurate (TAIC), Hexanediol Diacrylate (HDDA) and Tripropyleneglycol Diacrylate (TPGDA) influences the radiated PBS properties. PBS/HDDA blends with 20 kGy dose shows the highest in mechanical stability of this type of biodegradable resin. The surface morphology study and mechanical values have been used to correlate change in the structure of PBS upon degration.

1. Introduction

The crosslinking structure in the polymer can be effectively formed by EB radiation. Ionizing radiation produces an excitation of polymer molecules in the vicinity of the impinging radiation. The energies associated with the excitation are dependent on the irradiation dosage and voltage (velocity) of electrons. The interaction results in the formation of free radicals formed by dissociation of molecules in the excited state or by the interaction of molecular ions. The free radicals or molecular ions can react by connecting the polymer chains directly or initiating grafting reactions. EB radiation resulted in uniformly cured due to the full depth penetration of the electrons (Boye, 2008).Radiation of thermoplastic is generally aimed at introducing the desired amount of crosslinking or chain scission between reactive polymer molecules. Crosslinking will bring about an increase in tensile strength, elongation, modulus of elasticity, hardness and softening temperature. On the other hand, chain scission decreases these properties. Therefore, to find the optimum radiation dose is important to prevent further degradation. Chain scission during radiation can be prevented by addition of certain reactive groups because the reactive groups can transfer and dissipate the energy intermolecularly thus acting as an energy sink (Zainuddin et al., 1999). PBS is a type of aliphatic polyester that can be efficiently synthesized through condensation polymerization from the starting materials of succinic acid and butan-1,4-diol. It is a white crystalline thermoplastic polymer with a melting point around 90–120 °C (similar to LDPE), glass transition temperature of about -45 to -10 °C (between PE and PP), a tensile strength between PE and PP, and stiffness between LDPE and HDPE. PBS has excellent processing capabilities and can be processed on polyolefin processing machines at temperatures of 160–200 °C, into various products, such as injected, laminated, foamed, extruded and blown ones. It is a biodegradable plastic that has been carried out in order to overcome the environmental problems associated with synthetic plastic waste. Like a cellulose and paper, PBS is stable in the atmosphere but biodegradable in compost, wet soil, fresh water, seawater and

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activated sludge where microorganisms are presented. The crosslinking agents added into polymers can promote crosslinking over degradation process hence can enhance the strength of the materials. The presence of TMPTA, HDDA and TAIC as coagents are commonly used for radiation-induced crosslinking of polymers. Conversely, by EB-initiation, TPGDA appears clearly to be more reactive than HDDA, with an initial polymerization rate twice as large as that of HDDA. Meanwhile, TAIC/nylon6 blends has reported can be radiated further until 400 kGy optimum dose (Rytlewski, et. al. 2010). However, their performance might be the difference since the compatibility between the polymers is much more important. The aim of this article is to find the optimum radiation dose and provide the information regarding the influences of three types of crosslinker upon the radiated PBS resin. The product is expected to solve the environmental issue on current non-biodegradable plastic whilst enhancing the properties of PBS.

2. Materials and methods

2.1 Materials

Pelletized polybutylene succinate (PBS) Bionolle, grade 1010 was received from Showa High Polymer Co. Ltd., Japan. Chloroform (R&M Marketing Essex, UK) analytical grade was used. Hexanediol Diacrylate (HDDA) from Bayer, Germany, Triallyl Isocyanurate (TAIC) (Sigma Aldrich GmbH, Germany) and Tripropyleneglycol Diacrylate (TPGDA) from (R&M Marketing Essex, UK) were used as received.

2.2 Blending and sample preparation

The blends were prepared using Brabender Plastograph machine rotating at a speed of 50 rpm at temperature 115°C. For addition with cross-linking agents, only one dose was used which is 20 kGy. These cross-linkers were mix by wetting process first before process into the Brabender Mixer. The amount was varied with 0.5,1 and 2 % (w/w) using the same parameter. The process was conducted for 10 minutes and torque versus time curve for every blend was recorded. The blend samples then compress for 5minutes into sheets at 130°C. Samples for Flexural and impact test was using stainless steel mold (15 cm × 15 cm × 0.3 cm). For tensile test, a stainless-steel mold (15 cm × 15 cm × 0.1 cm) was used. All molded samples were cut into 7 standard test pieces using a Wallace die cutter.

2.3 Radiation of the sample

Radiation of the samples was carried out at Alutron Department, Malaysia Nuclear Agency. The molded sheets were placed in an aluminum container on a conveyor which able to move with a precisely controlled speed. The conveyor speed determined the radiation dose absorbed by the samples. During a single crossing of radiation zone, the samples absorbed a dose rate of 10 kGy per pass. The successive crossing of radiation zone caused an increase in the dose absorbed by the samples by the next 10 kGy. This way, the doses of 0, 10, 20, 40, 60, 80, 100, 120 and140 kGy were applied to the samples. The doses were controlled by a calorimetric method. All samples were irradiated with energy of 3 MeV and beam current of 5mA. After radiation, the tensile, flexural and impact were done to find the optimum curing doses for PBS. After the optimum dosage was determined, the process of blending was repeated by adding with different crosslinking agents.

2.4 Scanning electron microscopy

The morphology of the sample surface was investigated with high-resolution scanning electron microscopy (SEM), operated at an acceleration voltage of 20 kV and a working distance of 8-12mm. Electron micrographs were obtained on samples collected before and after biodegradation testing in soil (1 month). The morphology of the sample surfaced was examined using Quanta400. Prior to measurement, the specimens were coated with gold (purity, 99.9 %) in order to prevent electrical discharge.

2.5 Physical testing

Mechanical properties of the radiated sheet were tested on their tensile, flexural, melt flow index (MFI), heat deflection temperature (HDT) and impact strength. Tensile properties were measured using Toyoseiki with 1kN and crosshead speed of 10mm/min according to ASTMD 1822. Flexural properties were measured using Instron Universal Testing Machine 4301. The specimens were 12.7 mm wide and 1kN load was used. Three-point bending tests were performed with a span length of 43 mm at a crosshead speed of 1.3 mm/min referring to ASTMD 790. Izod impact strength notched with 2.54mm was done according to ASTMD 256. The specimen is held with a vertical cantilever beam and is broken by a single swing using 1J energy by the pendulum at a fix distance. HDT was carried out using Rayran HDT Vicat Softening Point according to ASTMD 648. Lastly, for MFI, temperature 190°C with load 2.16kg was done referring to ASTMD 1238.

3. Results and findings

3.1 Optimum radiation dose for polybutylene succinate

The optimum dose was determined by EB radiation at a dose range of 10–140 kGy. Upon radiation, the reactive group which is ester will undergo predominantly a crosslinking process and, as a result, a three-dimensional network of polymer chains is formed. Increase radiation dose will increase the crosslinking density marginally (Piah et al, 2016). The higher crosslink made the molecule become bigger and as a result, a stiffer and brittle sample was observed. The mechanical properties result for the dose range of 0–140 kGy are shown in Table 1. The optimum radiation dose at 20 kGy is confirmed by elongation at break, tensile strength, and impact strength. After radiation, elongation, tensile strength and Impact strength were improved until 20kGy followed by dramatically decrease at a higher dose. Intensive chain scission induced by radiation at above 20kGy reduce the length of PBS macro molecules hence result in decreasing in all mechanical stability test. The tensile strength of EB radiated PBS at low radiation dose slightly increased due to the formation of additional cross-linking in PBS from the production of mainly polymer radicals and hydrogen radicals. Increasing radiation dose also influenced the mechanical energy absorbed before fracture. For dose 20 kGy and above, the PBS has developed more crosslink in their microstructure but significantly alter the viscoelastic properties. Above 20 kGy, PBS exhibit brittle behaviors which reduce toughness to resist shock impact. Elongation shows a dramatic drop and tensile strength reduce marginally. It illustrates that higher radiation dose changes the structure of the sample by exhibit lower strain and brittleness. Thus, it can be concluded that PBS reached an optimum level at the radiation dose of 20 kGy. The dose with the most stable mechanical properties was chosen and added with the crosslinking agent.

Table 1: Effect of electron beam radiation on biodegradable plastic (PBS)

Dose (kGy)	Melt Flow Index (g/sec)	Elongation at break (%)	Tensile Strenght (MPa)	Tensile Modulus (MPa)	Impact Strength (J/M)
0	9.4 (0.26)	388.6 (11.2)	37.441 (1)	166.72 (3.91)	92.88 (1.4)
10	9.9 (0.154)	431.67 (5.4)	37.95 (1.59)	179.905 (4.91)	92.9 (0.89)
20	10.16 (0.23)	450 (4.49)	38.072 (0.7)	184.48 (6.9)	97.96 (1.01)
40	12.2 (0.273)	55.71 (1.94)	37.11 (0.49)	167.13 (12.3)	91.73 (1.9)
60	13.05 (0.28)	40 (3.9)	38.28 (1.1)	164.71 (17)	89.2 (2.34)
80	13.4 (0.21)	32.86 (3.53)	37.4 (1.25)	169.6 (12.04)	80.42 (2.91)
100	14.2 (0.259)	28.57 (5.5)	36.65 (2.8)	164.91 (13.4)	75.63 (2.31)
120	14 (0.22)	25.71 (2.94)	34.52 (2.19)	161.089 (11.8)	73.41 (2.09)
140	13.6 (0.31)	28 (6.7)	35.316 (3.21)	161.816 (16.1)	73.38 (2.86)

During crosslinking reaction, the average molecular weight of the chain increase thus causing a drop in melt flow. Table 1, depict the dramatic increment for melt flow index at 120 kGy figures that the reductions of PBS molecular weight. Intensive chain scission induced by irradiation at above 120 kGy reduces the length of macromolecules thus causing the drop in molecular weight. Degraded materials would generally flow more as a result of reduced in physical properties. Even if the chain already break, there is some bonding between the chain itself which reducing the movement of the molecule and make restriction of the flow.

3.2 Effect of crosslinking agent loading on mechanical properties

Crosslink density is a measure of the total links between chains in a given mass of material. Crosslinking was carried out through three types of crosslinking agent which is a molecule of two (TPGDA) and (HDDA) and molecules of three (TAIC) that are capable of reacting with the functional groups in the PBS chain (Capek, 1999). Contribution of crosslinking agent to increase crosslink density and mechanical properties were determined by Table 2. It shows that higher addition of crosslinking agent resulted in higher crosslink density (Ratnam, 2000). However, too much crosslinking may also lower the strain induced crystallization process. It is generally known that tensile strength and elongation at break depend on the degree of the strain-induced

crystallization, which in turn depends on the polymer chain length and the degree of cross linking. Table 2 depict that the dynamic mechanical properties obtained with increasing difunctional monomer HDDA content attributed to the acceleration of radiation induced crosslinking of the biodegradable plastic and proved that the blend are compatible. Whereas for TAIC, 1 % content showed the maximum amount of crosslink density which PBS could achieve. The increments of TAIC content only will only cause surface blooming and the excessiveness lead to lower mechanical properties. The surface morphology from Figures 1a depicts some of the TAIC powder which is immiscible during the blend. The high reactiveness of TAIC also lead to incompatibility since the functionality in the PBS is low. Therefore, it was enhancing the shrinkage process which yields to internal stresses and is responsible for the observed curling on flexible substrates. The TAIC was also reported can absorb acceleration until 100 kGy whereas the optimum dose for PBS is only 20 kGy (Piah, 2016). Aromatic parts of TAIC also alter the flexible thermoplastic PBS into a hard-brittle thermoset PBS. Therefore, the product will not melt and cannot be recycled. Consequently, when the composition of HDDA was increased, all the mechanical properties also increased. The same trend showed for TPGDA. The main factor to the value is the form of additives. TPGDA and HDDA are in liquid form whereas TAIC in fine powder form. The incorporation of liquid in PBS blend is more miscible and it can be proof from Figure 1a and b. Besides, HDDA and TPGDA are aliphatic difunctional monomers, they were more compatible with aliphatic polyester chain thus lead to better mechanical performances. Radiation creates free radical in the PBS chain and initiates crosslinking of the biopolymers. The reactive diluents like HDDA and TPGDA were used to absorb the radiation beam in order to generate free radicals that initiate the crosslinking network (Rytlewski et al, 2010). The improvement in mechanical strength properties proved the presence of unsaturation from an acrylic group was attached at the end of aliphatic polyester backbone chain. The increment in elongation proved that they impart more ductility but since the modulus shows a reduction, it became softer and the reduction in flexural strength depicts that the resistance toward bending stress is becoming lower due to the lower modulus. Therefore, the decrease in modulus has reduced it stiffness hence effect the sample surface tension.

Table 2. Effect of crosslinking agents on biodegradable plastic (PBS) mechanical properties

Formulation	Impact (J/M)	Elongation (%)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Flexural Strength (MPa)	Flexural Modulus (MPa)	HDT (°C)
PBS	92.88(2.3)	388.6(11)	166.7(3.19)	37.4(1)	44.45(0.7)	615.4(11.5)	97.4(1.3)
0.5 %TAIC	115.5(1.2)	394.3(4.8)	159.7(0.95)	38.9(1)	46.6(0.2)	645.7(5.6)	98.7(0.9)
1 %TAIC	88.3(2.5)	236.7(4.7)	160.8(9.4)	38.9(0.81)	43.93(0.8)	600.85(10)	101.5(0.7)
2 %TAIC	84.29(3.7)	171.1(1.6)	164.4(11)	36.5(0.98)	43.14(2.4)	606(25.6)	97.8(0.6)
0.5 %TPGDA	110.0(3.1)	453.3(1.6)	174.7(7.87)	38.3(2.03)	44.38(0.8)	615.5(11.6)	98.75(0.8)
1 %TPGDA	121.0(9)	460.0(10)	170(8.6)	39.5(1.37)	43.36(0.3)	607.23(7.7)	97.05(1.5)
2 %TPGDA	128.0(3)	723.0(9)	166.2(7.85)	48.8(1.01)	41.17(0.8)	556.94(8.5)	97.43(1.3)
0.5 %HDDA	108.5(0.3)	442.2(2.9)	183.7(6.5)	38.0(1.21)	44.96(0.5)	610.25(4.9)	99.17(1.1)
1 %HDDA	118.1(5.1)	725.4(8.3)	174.7(3.32)	48.1(0.54)	44.41(0.7)	604.5(12.7)	97.19(0.5)
2 %HDDA	145.3(3.5)	856(4.4)	171.4(1.52)	56.4(1.14)	41.78(0.4)	571.48(9.7)	97.6(0.7)

HDDA was expected to have higher mechanical strength compared to TPGDA due to its low molecular weight thus more compact blend occurred. Otherwise for TAIC, just 0.5 % addition has shown the increment in flexural strength and modulus. It figures that TAIC have alters samples properties becoming more resistance toward bending resistance. However, 1 and 2 % TAIC shows a reduction in tensile and flexural strength, elongation % and impact resistance. This might be due to the brittle behaviors reduce the ability of the sample to resist deformation with the load applied on it (Zainuddin et al., 1999). Impact strength was done to test the ability of every formulation to absorb applied energy. Increment of HDDA content showed that the HDDA imparts good molecular flexibility. With only 0.5 % loading, TAIC improved the modulus a lot but it also degrades impact properties. It illustrates that the increase in stiffness associated with decrease in impact strength. Besides, poor compatibility of TAIC particle during blending also lead to poor impact and others mechanical properties. HDDA and TPGDA are well dispersed in PBS allowing the blends to dissipate a significant amount of impact energy. Morphological observation indicates a finer dispersion of HDDA. From the Figures 1a, the particles are uniformly distributed in the PBS and do not give an indication of aggregation. Aggregates, such that the cracks will propagate easily and rapidly, causing premature failure. Table 1 shows the impact strength of the investigated samples. As the HDDA and TPGDA content increases, the impact

strength increases. These was probably due to the sufficiently high amount of polymer radicals produced that react with monomers at these doses. The increased tensile strength with HDDA amount was due to the slightly increased crosslinking in the amorphous PBS region that resulted in the production of polymer radicals and hydrogen radicals (Liu et. al. 2017). HDT were also tested to detect the temperature of the blends deforms under a specified load. For 2 % TAIC, to high crosslinking decrease its elongation percent. But, the high crosslinking is very useful during high temperature applications where it can stand until 101.5 °C in hot oil environment. Therefore, high temperature needs to break the crosslink and thus make it bend (Piah et. al. 2016). Since the HDT result was very marginal, the increasing of cross linking did not affect the HDT result.

3.3 Scanning electron microscopy

Figures 1a to 1f on SEM images shows the sample degradation surface before and after 2 month the soil burial without oxygen.

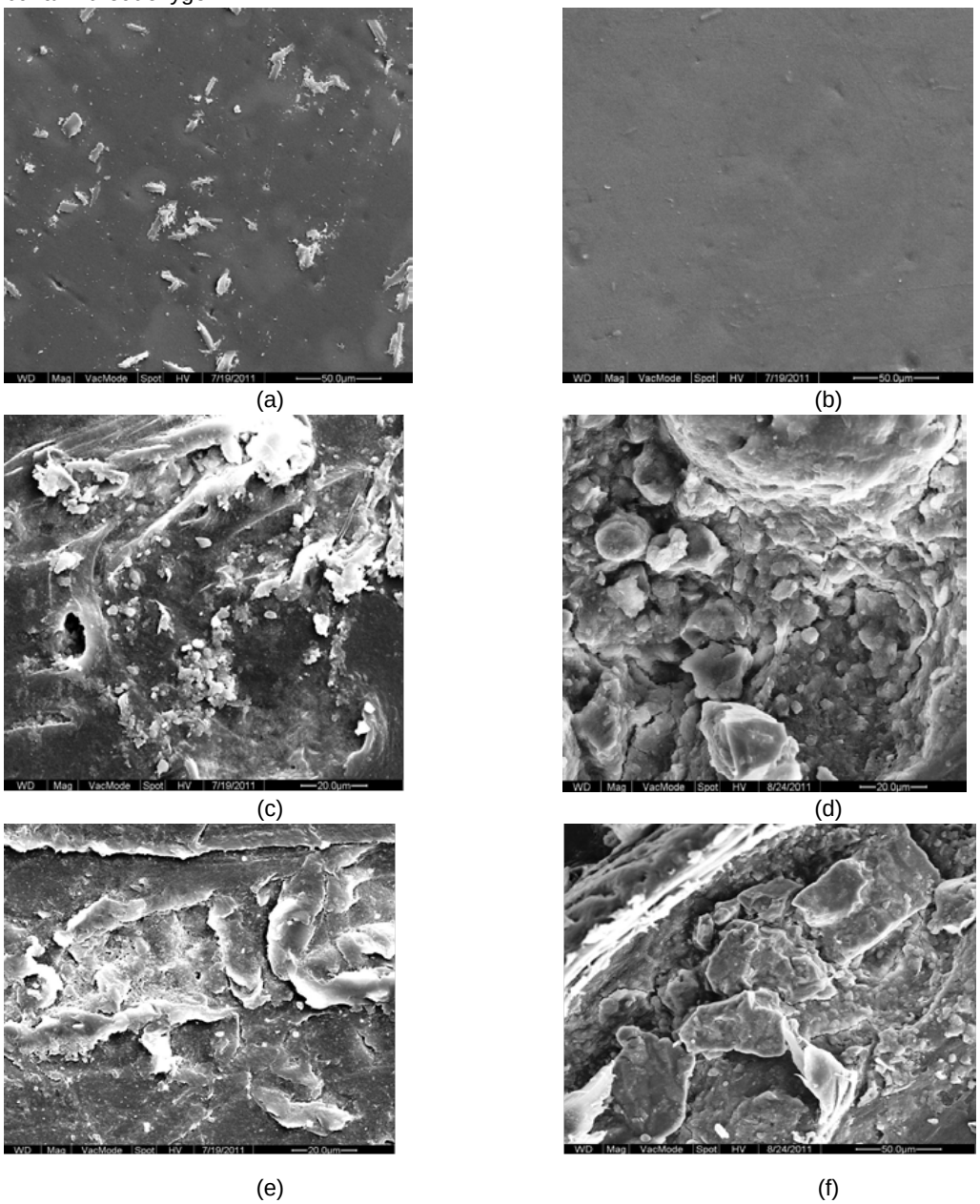

Figure 1: SEM micrograph of the samples before and after 2 months in natural soil burial (a) PBS/2 %TAIC before soil burial (b) PBS/2 %TPGDA before soil burial (c) PBS/2 % HDDA after soil burial (d) original PBS after soil burial (e) 2 % TAIC after soil burial (f) 2 % TPGDA after soil burial.

Before the soil burial test, the pure PBS presented a relative smooth and clear surface. The images were take on the surfaces because microbial erosion is likely beginning from the surface of polymer. It seen that for all sample, degradation already occur even in 2-month burial time resulting from microbial attack. For all buried samples, it shows that the microorganism is well growth on the surface, the surface was considerably eroded and partial defect formed on the surface. Only a few areas of original and the degradation caused a very rough topography, creating a larger surface area due to microbial attack. It illustrates that even for high crosslinked density sample, it still can be digested by microorganisms and has equal degradation rate to uncross linked PBS. It can be concluded that PBS is stable in the atmosphere but biodegradable in soil with the molecule breakdown or broken chains in the networks start less than 2 months.

4. Conclusion

Radiation influences the properties of polymer materials. These results explained that low doses of radiation can promote crosslinking over degradation reactions to the PBS polymer. Suitable radiation dose of polymer materials was needed to improve properties of materials thus suit the industrial application. The optimum radiation dose which PBS can absorb is 20 kGy and intensive chain scission induced by irradiation at above 20 kGy reduces the length of PBS macromolecules and thus cause a decrease in molecular weight, strength, and elongation at break. EB radiation above 20 kGy will just promote degradation and made the material brittle, hence higher dose for crosslink is not preferable. Addition of crosslinking agent influence the absorption efficiencies ability. Increasing addition of TAIC promotes brittleness due to its high reactiveness. 2 %TAIC shows marginal increment in HDT and 0.5 % TAIC depict the highest flexural strength and modulus. HDDA illustrate the highest toughness for properties like elongation, impact and tensile strength. Increasing the used of HDDA liquid make the sample become less stiff thus make it become more ductile. Overall in mechanical terms, HDDA and TPGDA produce less stiff properties but increase in toughness of the PBS. Overall, the used of electron beam radiation with the crosslinker agent have improved the PBS. The properties of PBS can be altered suitable with the applications and it will degrade when no oxygen occur hence reducing environmental problems caused by plastic waste.

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