

## SYNTHESIS AND THERMAL-STABILITY STUDY OF POLYBUTYLENE ITACONATE MODIFIED WITH DIVINYL BENZENE AND GLYCEROL

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### ABSTRACT

Polybutylene itaconate (PBI) for modification with divinyl benzene (DVB) and glycerol has been synthesized at 180 °C for 3 h via polycondensation of itaconic acid (IA) and butanediols using catalyst of Ti(OBu)<sub>4</sub>. Modification on PBI was done with addition of 15%, 20% and 25% DVB (w/w) using benzoyl peroxide. With glycerol, weight variations of glycerol:1,4-butanediol (BDO) in the synthesis were 10%, 30%, and 50% (mole/mole). PBI and PBI modified with DVB and glycerol were characterized with FTIR and TG-DTA. PBI showed a wavenumber shift from 1703 cm<sup>-1</sup> to 1728 cm<sup>-1</sup> of the C=O functional group from acid to ester. The DVB modification on PBI also showed that the intensity decrease of C=C stretching was due to the formation of crosslinking on the double bond. In the modification with glycerol, three dimensional networking on the polyester occurred through bonding between hydroxyl of glycerol and acid group of IA. Constant intensity of C=C stretching on polyester was seen. The thermal stability of PBI modified with DVB increased, accompanied by rigidity change of the structure. The thermal stability of PBI modified with glycerol decreased, caused by the decrease of regularity degree and the elasticity increase of the three dimensional structure of polyester.

**Keywords:** thermal stability; polybutylene itaconate; divinyl benzene; glycerol

### ABSTRAK

Polibutilena itakonit (PBI) untuk modifikasi divinil benzena (DVB) dan gliserol telah disintesis pada 180 °C selama 3 jam melalui polikondensasi asam itakonit (IA) dengan butanadiol dengan katalis Ti(OBu)<sub>4</sub>. Modifikasi pada PBI dilakukan dengan variasi 15%; 20% dan 25% DVB (b/b) menggunakan benzoil peroksida. Modifikasi dengan gliserol dilakukan dengan variasi mol gliserol: mol 1,4-butandiol (BDO) adalah 10:90, 30:70, dan 50:50. Analisis FTIR dan TG-DTA dilakukan terhadap PBI dan PBI termodifikasi DVB dan gliserol. PBI menunjukkan adanya pergeseran bilangan gelombang dari 1703 cm<sup>-1</sup> ke 1728 cm<sup>-1</sup> yang menandakan terjadinya perubahan gugus C=O asam menjadi C=O ester. Modifikasi DVB pada PBI menurunkan intensitas uluran dari gugus C=C yang dikarenakan terbentuknya ikatan silang pada ikatan rangkap dua dari PBI. Pada modifikasi dengan gliserol, percabangan yang terjadi pada poliester disebabkan adanya ikatan hidroksi dari gliserol dan gugus asam dari IA. Intensitas uluran C=C pada poliester terlihat tetap. Kestabilan termal dari PBI dengan DVB semakin meningkat, disertai perubahan rigiditas dari strukturnya. Peningkatan kestabilan disebabkan adanya ikatan intermolekular polimer tiga dimensi dan adanya jembatan aromatik dari DVB. Disisi lain, kestabilan termal dari PBI pada penambahan gliserol menurun, disebabkan turunnya derajat keteraturan dari struktur tiga dimensi poliester dan meningkatnya keelastisitasan dari struktur tiga dimensinya.

**Kata Kunci:** Kestabilan termal; polibutilena itakonit; divinil benzena; gliserol

### INTRODUCTION

Chemical modifications on polymers are usually done to obtain materials with physical properties that are more suitable for specific applications or for some purposes. Substance addition of a polymer with specific agents is able to be done by further reactions after

polymerization or during polymer formation. These reactions are needed in order to bind substances or additives on the polymer framework so that modification of polymer occurred. The chemical-modification reaction is selected based on kinds of binding reaction of the additives or substances on the polymers. It is also important to modify a polymer that

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is done during polymer formation based on the mechanism of the polymerization. The chemical modification during addition polymerization or polycondensation follows condition-suitable with the addition reaction or condensation reaction. This modification also can be carried out after the main polymerization accomplished, if the mechanism or condition of the main and further reaction is completely different. Aliphatic polyesters are able to be modified via addition reaction to bind branches on the aliphatic group. The presence of crosslinking agent influences the change of the three dimensional structure of the polyesters. The addition of the branches on aliphatic polyester is possible if unsaturated group or double bond in the chain backbone available. The chemical modification of polyester can be done with two possibilities, during the main polycondensation and by further addition reaction of the double bond with free-radical catalyst. Generally, the double bond group on a polyester backbone is able to be modified with some agents of epoxy, hydroxyl or carboxyl [1]. Synthesis of the aliphatic polyester requires a reaction condition of the same mole of diacid with diol, as in the reaction of polybutylene itaconate [2]. Reaction equilibria of the polycondensation are able to be reached if the quantity of monomers in a synthesis equal [3]. This condition may affect a polymerization accomplished and molecular weight of a polymer increases [1].

Itaconic acid (IA) is one of the promising natural substances classified into organic acid obtained by a fermentation of carbohydrate from *Aspergillus* fungi [1,4-5]. IA contains dicarboxylic and a double bond, in which one of the carboxylic group is conjugated to methylene group. The use of this acid is mainly needed for industries, such as polyester, plastic, coating, bioactive substances for agriculture, pharmacy, drugs and some other industrial products [5].

Polyester is usually formed by polycondensation reaction of diacid or its derivatives with diols. Aliphatic polyester is one of interesting polymers because of the biodegradability and thermoplastic. However, this physical-chemical property of the end product and the monomer availability for the production are as limitations in the commercial use. Aliphatic polyester that is thermoplastic can be modified as a thermoset polyester. This modification is aimed to obtain physical-chemical properties that are different from the common property of polyester, such as harder, more rigidity and better tensile strength and thermal stability [6]. One of the advantages of aliphatic polyester is that the possibility of the polymer to form three dimensional network by addition of crosslinking agents such as styrene, divinyl benzene, vinyl toluene, dichloro styrene, methyl methacrylate, allyl carbonate [7], ethylene glycol dimethacrylate, sucrose, and glycerol [8].

Monomer of styrene can be used in the modification of rigid polyester via free radical polymerization. Styrene has one reactive vinyl group so that a formation of networking with vinyl group from itaconate part of polyester is possible [6]. Divinyl benzene (DVB) is non polar substance and classified as derivate of benzene with two vinyl groups on the meta and para position [7]. A substance with aromatic group commonly has good resistance towards high temperature during heating, because they tend to form aromatic substances. This can be probably as a reason why polymers with aromatic substances tend also to have more resistance toward high temperature [8].

Glycerol has three hydroxyl groups that are bounded on three aliphatic carbon as two primary alcohol and one secondary alcohol [9] of  $\alpha$ ,  $\beta$  and  $\gamma$  carbon atoms. Three hydroxyl groups are reactive enough to form an oligomeric block or branch polymer to increase elasticity of polyesters. These branches have a correlation with the thermal stability of a polymer. More branches of a polymer, the thermal stability decrease [10-11].

The aim of the study is to synthesis polyester of PBI with the present of titanium butoxide. Modifying polyester is then done with DVB and glycerol to obtain thermoset polyester. Thermal behavior of the polyester is tested to identify the thermal stability of polyester after modification.

## EXPERIMENTAL SECTION

### Materials

Materials used for the study were itaconic acid p.a grade (Sigma-Aldrich Chemical), 1,4-butanediol (BDO) p.a grade (Merck), divinyl benzene p.a grade (Merck), glycerol p.a grade (Brataco), p-methoxyphenol p.a grade (Merck), Ti(OBu)<sub>4</sub> p.a grade (Aldrich), toluene p.a grade (Merck), acetone p.a grade (Merck), ethanol p.a grade (Merck), benzoyl peroxide p.a grade (Merck), Nitrogen gas.

### Instrumentation

FTIR used was from Shimadzu type 820431. TG-DTA used was from Shimadzu type DTG 60 H.

### Procedure

#### Synthesis of PBI

PBI was synthesized with 13.01 g IA, 9.00 g BDO, 0.22 g p-methoxyphenol, 0.24 mL catalyst of Ti(OBu)<sub>4</sub> in 2 mL toluene. Synthesis was done in a three necks flask equipped with thermometer and magnetic stirrer. Polyester synthesis was done through

polycondensation reaction in nitrogen atmosphere, in which water as side product was pushed out with nitrogen stream and cooled with condenser. The nitrogen stream was controlled about 2 bubbles per second and 4-6 bubbles per second after water began out of the flask. The mixture was heated at about 180 °C for 3 h. The product was cooled at room temperature.

#### **Modification of PBI with DVB**

Modification of PBI with DVB was as further synthesis that was done after the main synthesis of PBI. Powder form of 10 g PBI yielded from first synthesis was removed in a 250 mL flask equipped with reflux condenser, thermometer and magnetic stirrer. Synthesis was done in nitrogen stream controlled with silicone oil about 2 until 6 bubbles per second. Addition of DVB was done with variation of 15%, 20% and 25% w/w PBI and benzoyl peroxide about 1% w/w PBI in 1 mL acetone. Reflux was done at 100 °C for 3 h as described in the previous procedure. Product was cooled at room.

#### **Modification of PBI with glycerol**

Modification of PBI with glycerol was done during the main synthesis of PBI by addition of a small quantity of glycerol into BDO that was reacted with IA. The condensation reaction was done with 7.72 g BDO/0.87 g glycerol (90% mole BDO:10% mole glycerol). It was done also for the addition of 30% and 50% glycerol. The product was cooled at room temperature.

#### **Acid number determination**

The determination of acid number was carried out by titration of certain milligram of polyester using 0.1 M potassium hydroxide solution which was firstly standardized.

Dilution of 0.50 g PBI with ethanol/toluene (1:1) was done up to 25 mL with volumetric flask. Polyester solution was removed exactly 5 mL into erlenmeyer and added 2-3 drops 1% PP indicator. Titration with 0.1 M potassium peroxide was stopped until reddish solution occurred. The acid number was determined based on the potassium hydroxide needed for the titration and was done five times.

#### **Intrinsic viscosity**

Sample of 4.0 g/dL PBI was made by a dilution of 0.40 g polyester up to 10 mL. Some solutions with concentration of 2.0, 1.0, 0.5, 0.25 g/dL were also made for this test. Each 2 mL solution was tested with Ostwald viscometer for the flow time of the solution from the upper to the bottom line. The viscosity test of the chloroform was also done before the test of sample solution. A value of intrinsic viscosity was determined by means the flowing time of each solution.

#### **FTIR characterization**

For the characterization, polyester tested was firstly mixed with KBr and pressed to a pellet form. Analysis was done in the range area of 4000-400  $\text{cm}^{-1}$  with scanning resolution 2  $\text{cm}^{-1}$ .

#### **TG-DTA characterization**

Polyester sample was packed in the aluminum pan streamed with nitrogen gas. Analysis condition was done with heating rate 10 °C/min, gas flow 50 mL/min from 30 °C until 600 °C.

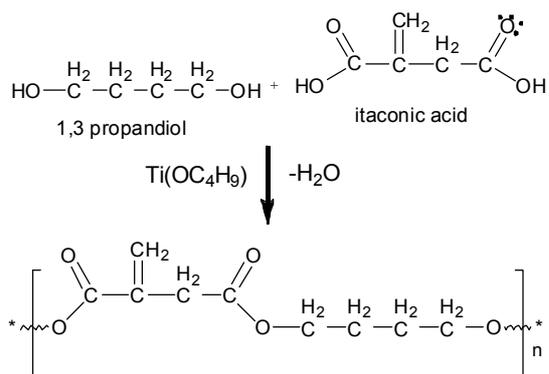
## **RESULT AND DISCUSSION**

### **Synthesis Product of PBI**

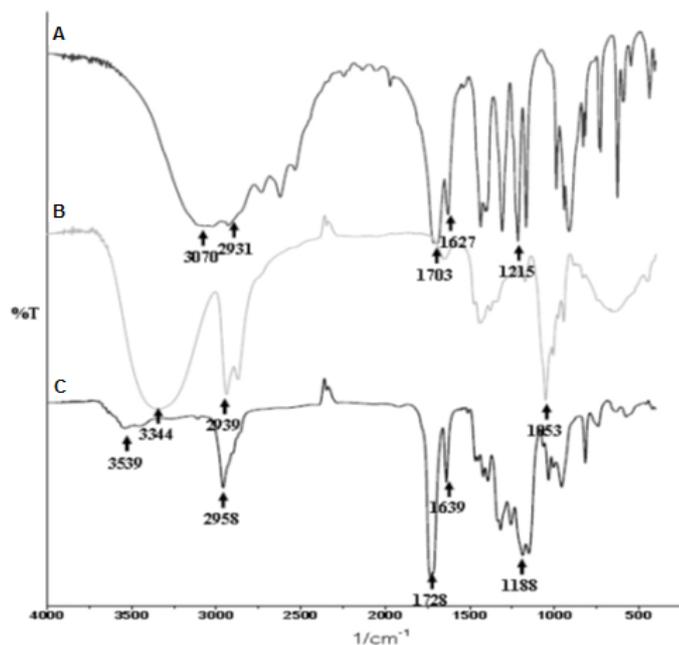
Reaction of IA and BDO with the present of titanium (IV) butoxide in the reactor yielded water as side product (see Fig. 1). The water should be excluded from the system with nitrogen or vacuum. Physical profile of PBI after polycondensation from IA and BDO for 3 h showed a yellowish viscous form that is still able to flow if tilted. This product was proven by wavenumber shift of carbonyl group (C=O stretching of acid) on 1703  $\text{cm}^{-1}$  to 1728  $\text{cm}^{-1}$  (C=O stretching of ester). The most important of this polycondensation is that double bond of the polyester should be kept not involving in any reaction. That is why, this reaction was kept at 180 °C so that inter crosslinking reaction of each monomer is able to be avoided. Beside, the addition of p-methoxyphenol was done to compensate heat transfer during reaction effecting any reaction of the double bond. The double bond (C=C stretching) of polyester was still showed by the wavenumber 1639  $\text{cm}^{-1}$  (see Fig. 2).

The acid number of PBI was determined titrimetrically based on the sum of the acid available that is equal to the quantity of KOH/NaOH needed to neutralize 1 g sample using PP indicator [12]. The acid number of polyester investigated was the total concentration of remaining carboxylic group of itaconic acid after synthesis. During the reaction, the carboxylic group reacts with the hydroxyl group and the quantity of both active groups decrease as polymerization occurred. Intramolecular interaction during condensation of monomers in the stage of the polymer growth is possible [13]. The acid number of the PBI synthesized was 34.97 mg/g. The acid number of the polymer correlates to the physical property of the polymer. The acid number of a polymer increases, it tends to fragile [12].

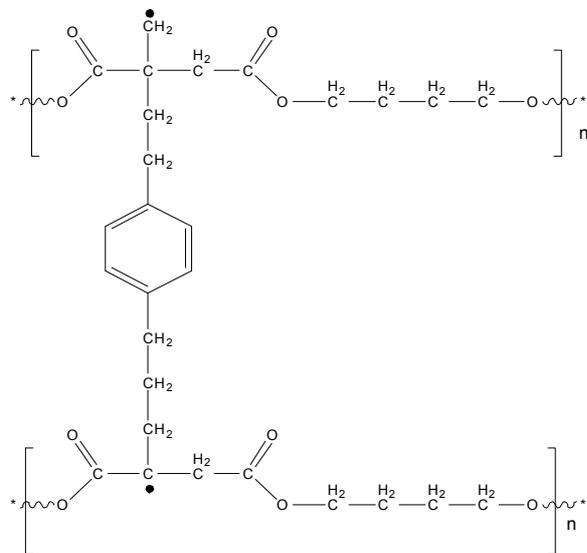
Intrinsic viscosity ( $\eta$ ) of PBI was determined by plotting  $\eta$  specific vs. polymer concentration. This data is useful to predict the molecular weight of the polyester if gel permeation chromatography (GPC) is



**Fig 1.** Reaction of 1,4-butanediol and itaconic acid



**Fig 2.** FTIR spectra of (a) IA, (b) BDO, and (c) PBI



**Fig 3.** Structure of PBI-DVB

not available. Generally, the rigid polymer has viscosity value higher than flexible ones [14]. The viscosity intrinsic of polyester obtained was 0.147 dL/g.

### Synthesis Product of PBI with DVB and Glycerol

In the modification of PBI with DVB, the double bond of polyester should be reacted with vinyl groups of DVB. This means that an aliphatic part of polyester was linked with such aromatic bridge of DVB to other aliphatic groups from other polyesters. This crosslinked polyester has clearly different profile with the previous PBI, especially the hardness of polymer. Structure of PBI after modification with DVB is shown on Fig. 3. The aromatic bridge of polyester was showed by characteristic absorption wavenumber on weak absorption on  $3109\text{ cm}^{-1}$  (C-H aromatic stretching). Nevertheless, the double-bond absorption of allylic part of polyester still weakly remained, in which the intensity on  $1637\text{ cm}^{-1}$  (C=C stretching) was very weak seen, compared to previous PBI. This absorption from this double bond was caused by the absorption of trace double bond remaining that did not react with DVB. In this modification, the self addition reaction between DVB was also possible. That is why the addition of DVB during synthesis was done carefully and step by step followed by ceaseless stirring. The C=C stretching was looked smoother not only due to the decrease of double bond on the itaconate chain but also the overlapping of the absorptions with the C=C stretching from DVB possibly occurred. The quantity of DVB added into PBI caused the intensity of C=C stretching seen on the spectra increased. The shift of wavenumber of spectra indicating the physical blending of the heterogeneous polyester was not clearly seen as (see Fig. 4).

The PBI addition with glycerol during the reaction caused the atactic structure of polyester as random reaction easily occurred between hydroxyl group and acid group, no matter it belongs to BDO or glycerol. Physical profile of PBI after modification with glycerol is shown on Fig. 5. The linearity of the polyester chain was disturbed by the present of glycerol because the condensation of three hydroxyl groups with diacids made a possibility that is each of three hydroxyls in a glycerol can react with three different itaconic acids. This condensation caused three dimensional networking of polyester occurred and affected a shape memory to the polyester. Compared with itaconic acid spectra, the polyester showed the wavenumber shift from  $1703\text{ cm}^{-1}$  (C=O stretching) of itaconic acid to  $1728\text{--}1732\text{ cm}^{-1}$  of polyester. The absorption on  $2960\text{ cm}^{-1}$  showed the C-H stretching from polyester, as also mentioned from the other study [10]. The C=C stretching on  $1650\text{--}1600\text{ cm}^{-1}$  of the polyester was still

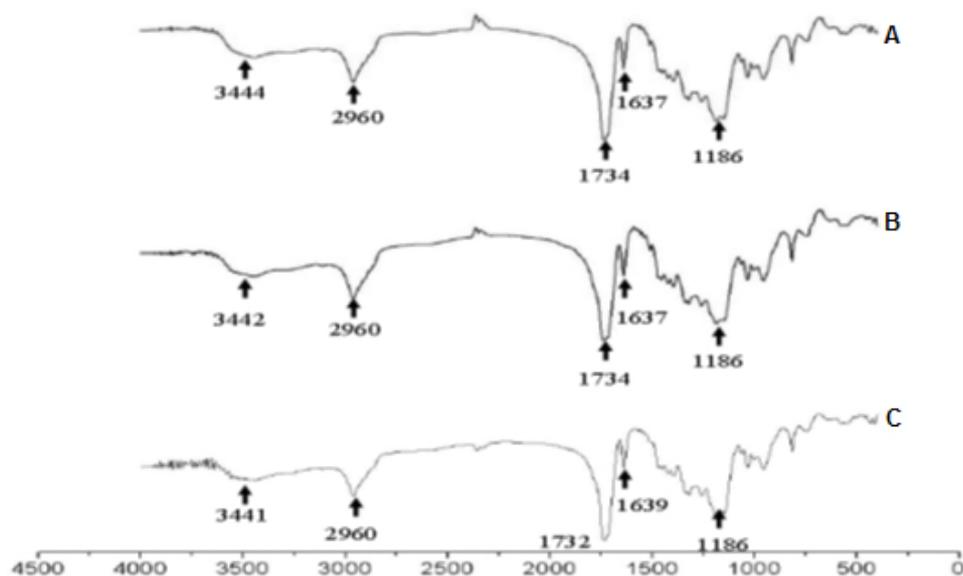


Fig 4. FTIR spectra of PBI with DVB (a) 15%, (b) 20%, (c) 25%

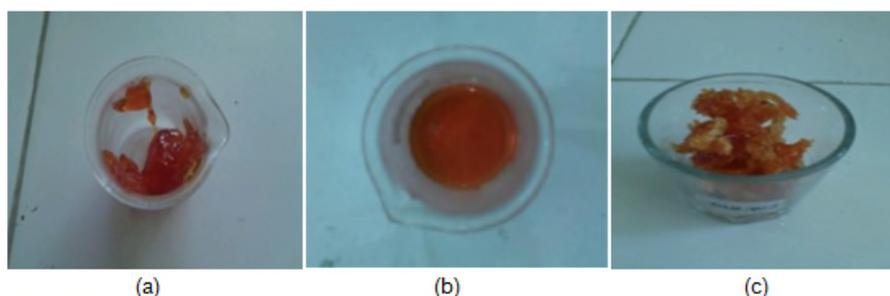


Fig 5. Physical profile of PBI after addition with (a) 10%, (b) 30% and (c) 50% glycerol

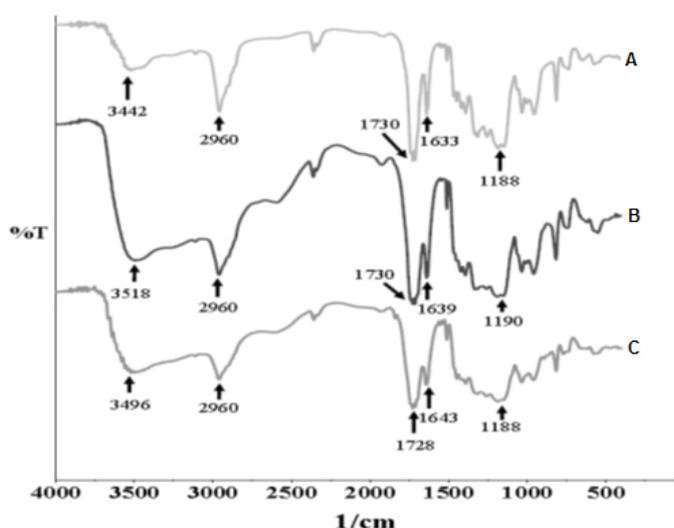


Fig 6. FTIR spectra of PBI added with (a) 10:90, (b) 30:70 and (c) 50:50 (mole IA/ mole glycerol)

clearly seen as polycondensation did not affect on the double bond of the itaconate chain and reaction just occurred between hydroxyl and acid groups (see Fig. 6).

#### Thermal Stability Study of PBI Modified with DVB and Glycerol

In general, a lost of 5% mass after heating analysis is considered as the begin of the significant lost of the mass. The lost of 5% unmodified PBI mass began at 270 °C (see Fig. 7). After modification with DVB, thermogramm of TG-DTA showed that DVB modified PBI has different thermal stability compared to unmodified one. Here, the addition of the more percentage of DVB indeed increased the thermal stability of the polyester as  $T_{max1}$  and  $T_{max2}$  increased [1,12]. In general, the addition of DVB increased also the temperature point of  $T_{5\%}$ ,  $T_{10\%}$ , and  $T_{50\%}$  that was used as points for the thermal-stability comparison of between polyesters. As seen on Fig. 8, the thermal stability of polyester modified with 25% DVB was looked the most significant compared to with fewer DVB ones. This was mostly caused by the quantity of the three dimensional networking of aliphatic polyester increased due to the increase of DVB bonding with itaconate chain via aromatic bridge. The increase of the thermal stability was theoretically caused by the higher

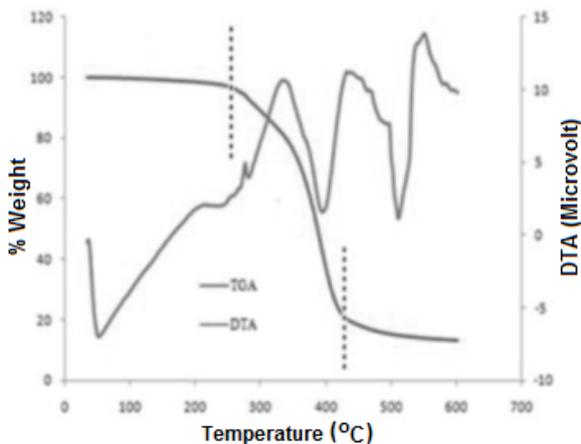


Fig 7. TG-DTA Thermogramm of PBI

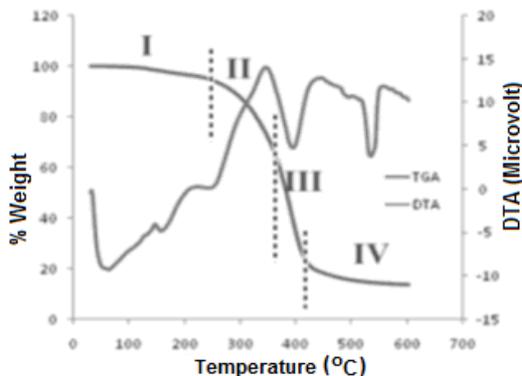
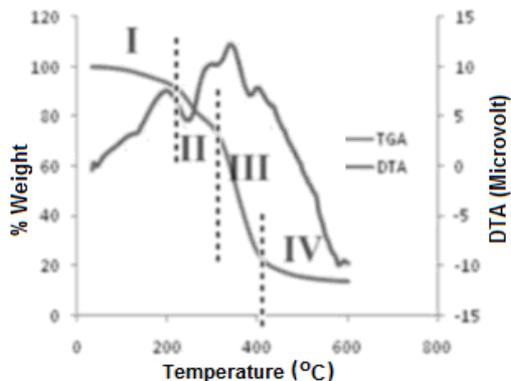
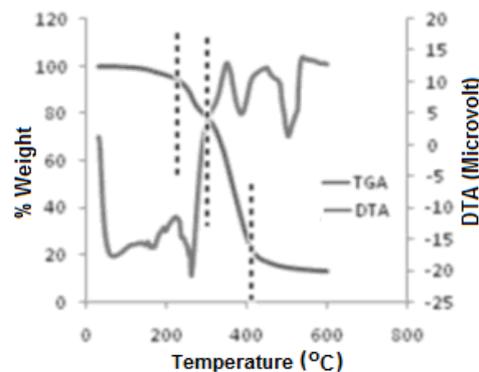


Fig 9. TG-DTA thermogram of PBI added with (a)10:90, (b) 30:70 and (c) 50:50 (mole IA/ mole glycerol)

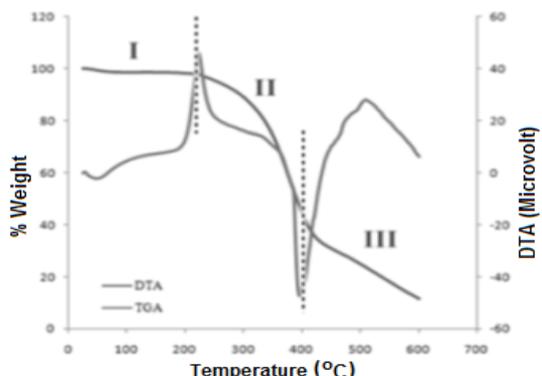
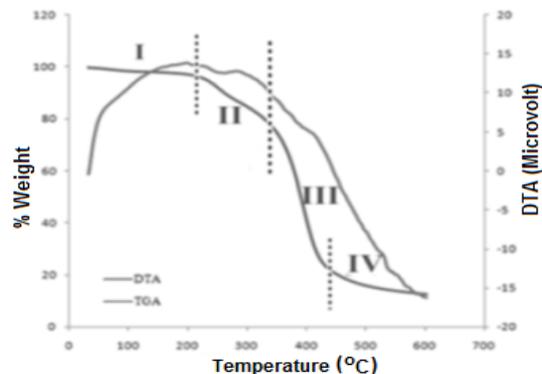
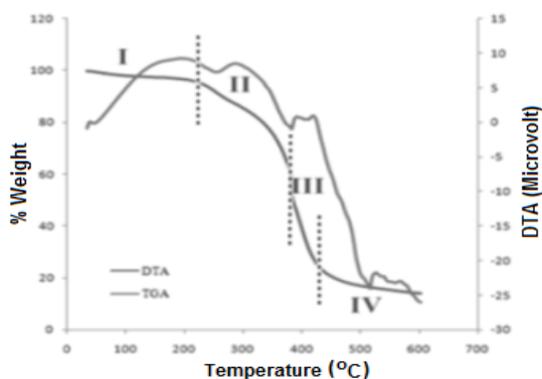


Fig 8. TG-DTA thermogram of PBI added with DVB (a) 15%, (b) 20%, and (c) 25%

degree or longer polymer chain, higher crosslinking degree and higher rigidity of the polymer [15].

As seen on Fig. 8, addition of 5% DVB towards PBI showed that four changes of the mass and thermal depicted by curve change occurred. First change was showed at 30-201 °C, as polyester mass decreased about 3% exothermically due to H<sub>2</sub>O and crystal transition on polyester occurred. Second change occurred at 201-327 °C due to degradation of polyester chain through decomposition of carboxyl exothermically occurred. Third change was at 327-413 °C due to degradation of ester group of polyester occurred. The fourth change was at 413-600 °C due to the decrease of 11% mass of carbon group of polyester occurred.

The different result was obtained with the addition of PBI with glycerol. Thermal stability of polyester decreased with the quantity increase of the glycerol added. Thermal stability of the polyester decreased due to the present of more glycerol. This is related to the decrease of crystallinity of polyester as glycerol changed three dimensional structure of the polymer and caused the amorphicity increased as polyester with more random three dimensional forms affected the irregularity of the structure. The linear form of a polymer has more regularity of three dimensional structures. The better crystallinity of linear polyester commonly increases the thermal stability of a polymer [10]. The polymer with more branches causes crystallinity of the polymer decreased and biodegradability increased. As seen on Fig. 9, the addition of 50% glycerol affected a structure with the highest irregularity compared to any other additions.

As seen on Fig. 9, PBI with glycerol showed three thermal changes during heating. First change was at 30-241 °C indicating the decrease of 5% mass endothermically occurred due to the removal of H<sub>2</sub>O and melting of polyester occurred. Second change was at 241-350 °C indicating degradations of ester group within polymer chain occurred. Third change was above 350 °C indicating degradation of polyester, especially carbons atom of aliphatic group occurred. Compared to PBI unmodified, the polyester modified with glycerol has different transition curve on thermogram. It means that addition of glycerol influenced the thermal stability of PBI.

## CONCLUSION

Modification of PBI with DVB and glycerol affects the thermal stability of the polyester. The thermal stability effect of PBI depends on the quantity of the crosslinking agent added in a polyester and is accompanied by other physical properties (viscosity and hardness of polyester). The increase of DVB quantity added in PBI affects on the increase of thermal stability of polyester. The increase of glycerol quantity added in

PBI affects on the decrease of thermal stability of polyester.

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