Mechanical Enhancement of Biodegradable Poly(butylene succinate) by Biobased Polyamide11

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Abstract. Biodegradable poly(butylene succinate) (PBS) was melt blended with biobased polyamide11, which an epoxy-based chain extender, Joncryl ADR-4300, was added to improve the blend compatibility. Mechanical properties of the blends were evaluated by tensile and impact testing. The blends were characterized by Fourier transform infrared spectroscopy, Differential scanning calorimetry and Thermogravimetric analysis. Morphology was investigated by Scanning electron microscopy. It was found that morphology of the immiscible blends with polyamide11 less than 50 wt% was a sea-island structure. Adding the chain extender confirmed better chemical compatibility in the blends evident by smaller dispersed domain sizes and less pullout. The blends with higher polyamide11 content increased Young’s modulus following the rule of mixture, however, the rigidity was reduced when adding the chain extender. It was interesting to observe that impact strength of the blends with polyamide11 content higher than 30 wt% was enhanced significantly with the presence of chain extender, although tensile strength and elongation at break were reduced. The crystallization temperature of PBS increased with higher polyamide11 content due to the nucleation effect, although the degree of crystallinity was in the same range. The thermal degradation temperature of the blend was shifted to higher temperature confirming the chain extension reaction occurred.

Keywords: Poly(butylene succinate); polyamide11; chain extender; morphology.
1. Introduction

Plastic materials have become a major role in modern lifestyle due to easy modification for desired application, light weight, toughness, environmental stability, and long-lasting service life. Due to these advantages, the plastic industries have been growing to be one of the industry sectors that are important to the sustainable development. Unfortunately, raw materials for plastic production come from non-renewable petroleum which possibly cause the shortage of raw material supplies in the future. Nowadays, the plastic waste after service life is the main cause of waste pollution to the environment due to too many consumption worldwide and poor waste management. One of solutions to the problem is replacing petroleum-based plastics with biobased plastics, which could reduce carbon footprint, green-house gases, and moves toward the sustainable development based on renewable resources.

Bioplastics could be categorized into two groups [1]. The first group is called “biodegradable plastics” that can be digested by bacteria via the fermentation process and transformed materials into carbon dioxide gas (CO₂), water, and low molecular weight organic substance. These organic substances should not be toxic to the growth of plants when they are buried in soil. Examples of these plastics are poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and poly(butylene adipate terephthalate) (PBAT). The other group is called “biobased plastics” which are derived from renewable materials, but they could not be biodegradable similarly to the first group. Examples of these plastics are bio-polyethylene (Bio-PE), bio-poly(ethylene terephthalate) (Bio-PET), and polyamide11. Since Thailand is one of the leading countries for the agricultural products, we have high potential to produce bioplastics which would drive the country’s industrial sector to the circular economy.

Poly(butylene succinate) (PBS) is one of biobased plastics that has been used to produce films for food packaging or mulch films for agriculture, coating layer on paper cups, plastic sheets, etc. It is expected in the future to apply in engineering applications such as electronics. Although PBS is flexible, tough, and can be processed easily similar to polyolefin, it has quite low tensile strength compared to petroleum-synthesized thermoplastics used to produce electronics products. Thus, PBS has been improved tensile strength by blending with other high-strength biopolymers such as poly(lactic acid) [2] or compounding to be nanocomposites [3]. Polyamide11 or nylon11 is an interesting candidate for PBS to improve mechanical properties. This biobased polymer is derived from castor oil which has high tensile strength, good resistance, and high impact strength, however, it is not biodegradable. Therefore, melt blending polyamide11 into PBS would prompt the blend for wider applications. Moriyama et al. [4] blended PBS with polyamide11 which they reported that the blend was an immiscible blend. The phase separation was clearly seen that the mechanical properties of the blends were reduced. They suggested that the interfacial adhesion between phases should be improved.

In this research, PBS was designed to be the main matrix and melt blended with polyamide11 in various weight ratios (up to 50 wt%) in order to investigate mechanical and thermal properties of the blends. Since PBS and polyamide11 had different functional groups that resulted in the immiscible blend, a multifunctional epoxyic compatibilizer [5] was incorporated in the melt blending in order to improve the interfacial interaction via the chain extension reaction. This soybean-based compatibilizer would act as a chain extender that linked the condensation polymers resulting the increase of melt viscosity from relatively higher molecular weight of polymers from the chain extender reaction [6]. The influence of the chain extender on mechanical and thermal properties of the PBS/polyamide11 blends was evaluated.

2. Experimental

2.1. Materials

Poly(butylene succinate) or PBS (BioPBS™ FZ91 PM, a density of 1.26 g/cm³, a melting temperature of 115°C, and a MFI of 5 g/10 min @190°C, 2.16 kg) pellets were purchased from PTT Biochem Co. Ltd., Thailand. Polyamide11 or nylon11 (Rilsan® BECNO BLACK TL, PA11, a density of 1.03 g/cm³, a melting temperature of 189°C, and a MFI of 30 g/10 min @235°C, 2.16 kg) pellets were purchased from Arkema Innovative Chemistry, France. This grade consisted of heat/light stabilizer and lubricant. An epoxy-based chain extender, Joncryl ADR-4300, was kindly supplied by O-BASF Corporation, Germany. It had a molecular weight of 5500 and an epoxy equivalent weight (g/mol) of 445. The chemical structures of PBS, nylon11, and Joncryl ADR-4300 are presented in Fig. 1.

![Chemical Structure of PBS, Nylon11, and Joncryl ADR-4300](https://engj.org/)

Fig. 1. Chemical structure of PBS (A), nylon11 (B), and Joncryl ADR-4300 (C).

2.2. Melt Blending and Specimen Fabrication

Prior to melt blending, PBS and nylon11 pellets were dried in an air-circulating oven (Model FD53, Binder, Germany) at 60°C and 80°C for 6 hours, respectively.
Table 1 summarizes abbreviation and composition of samples prepared and tested in the research. The melt blending was carried out in a co-rotating twin-screw extruder (SH-J25, Yongteng, China) using a screw speed of 40 rpm. The barrel/die temperature profile was set at 140-150-160-160-170-185-190-200°C. The extrudate was water cooled, pelleted, and dried in an air-circulating oven (Model FD53, Binder, Germany) at 70°C for 5 hours. Dried pellets were kept in zip-lock plastic bags and stored in a sealed plastic box equipped with silica gel bags to prevent moisture pick-up. Dogbone specimens (ASTM-D638 Type I, a narrow-section width of 12.8 mm and a thickness of 3.25 mm) and rectangular specimens (ASTM-D790, a length of 126.5 mm, a width of 12.5 mm and a thickness of 3.25 mm) were fabricated using an injection molding machine (BA250CDC, Battenfeld, UK). Neat PBS, neat nylon11, and the PBS/nylon11 blend specimens were fabricated using the barrel/nozzle temperature about 200-210°C, while neat nylon11 specimens had to be fabricated at 240°C.

Table 1. Abbreviation and composition of samples.

| Abbreviation | PBS (wt%) | Nylon11 (wt%) | Joncryl ADR-4300 (phr) |
|--------------|-----------|---------------|------------------------|
| P100         | 100       | 0             | -                      |
| P9N1         | 90        | 10            | -                      |
| P8N2         | 80        | 20            | -                      |
| P7N3         | 70        | 30            | -                      |
| P6N4         | 60        | 40            | -                      |
| P5N5         | 50        | 50            | -                      |
| N100         | 0         | 100           | -                      |
| P9N1J0.5     | 90        | 10            | 0.5                    |
| P8N2J0.5     | 80        | 20            | 0.5                    |
| P7N3J0.5     | 70        | 30            | 0.5                    |
| P6N4J0.5     | 60        | 40            | 0.5                    |
| P5N5J0.5     | 50        | 50            | 0.5                    |
| P9N1J1.0     | 90        | 10            | 1.0                    |
| P8N2J1.0     | 80        | 20            | 1.0                    |
| P7N3J1.0     | 70        | 30            | 1.0                    |
| P6N4J1.0     | 60        | 40            | 1.0                    |
| P5N5J1.0     | 50        | 50            | 1.0                    |

2.3. Characterization and Testing

Morphology of cryo-fractured specimens was examined using a Scanning electron microscope (SEM, TM3030, Hitachi, Japan). The fractured surface was gold/platinum coated prior to inspection to avoid electrostatic charging. The gold/platinum coating was performed by a sputter coater (Model SC7620, Quorum Technologies, UK) using a testing condition that used an electricity input of 20 mA, a pressure of 10⁻¹ mBar and a sputtering time of 45 second.

Next PBS, neat nylon11, Joncryl ADR-4300, and PBS/nylon11 blends were characterized functional groups by a Fourier transform infrared spectrometer (FTIR, VERTEX70, Bruker, USA). Pellets and KBr powder were dried thoroughly in an air-circulating oven (Model FD53, Binder, Germany). Then, they were mixed in the weight ratio of 1:9 (sample:KBr) and pressed by a hydraulic presses (Model 3392, Carver Inc., USA) using a hydraulic pressure of 10,000 Bar for 2 mins to obtain KBr discs for characterization.

Tensile properties of neat PBS, neat nylon11, and PBS/nylon11 blends were evaluated in accordance to ASTM-D638 using a universal testing machine (Model 5969, Instron Engineering Corporation, USA). The tests were carried out using a crosshead speed of 50.8 mm/min. Ten specimens were tested, which the averages and standard deviations of Young’s modulus, tensile strength, and elongation at break were calculated.

Impact strength of neat PBS, neat nylon11, and PBS/nylon11 blends was determined in accordance to ASTM-D256 (notched Izod impact test) using an impact tester (Ceast 9050 Pendulum Impact System, Instron Engineering Corporation, USA). The pendulum weight was 25 Joule. Ten specimens were tested which the averages and standard deviations of impact strength were calculated.

Thermal property analysis of neat PBS, neat nylon11, and PBS/nylon11 blends was evaluated using a differential scanning calorimeter (Pyris 1, Perkin Elmer, USA) under nitrogen atmosphere. Sample weight was about 5-10 mg. The samples were tested in a heat-cool-reheat mode. Temperature scan was performed from 50°C to 200°C with a heating rate and a cooling rate of 10°C/min. The crystal melting temperatures (Tm) and the crystallization temperatures (Tc) were reported. The degree of crystallinity (Xc) was calculated using Eq. (1).

\[
\% X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \tag{1}
\]

where w was weight fraction of PBS or nylon11 in the composite, \(\Delta H_m\) was melting enthalpy of sample (J/g), and \(\Delta H_m^0\) was either melting enthalpy of 100% crystalline PBS (110.3 J/g) [7] or of 100% crystalline nylon11 (206 J/g) [8].

Thermal stability analysis of neat PBS, neat nylon11, and the PBS/nylon11 blends was evaluated using a Thermogravimetric analyzer (TGA7, Perkin Elmer, USA) under nitrogen atmosphere. Sample weight was about 5-10 mg. Temperature scan was performed from 50°C to 600°C with a heating rate of 10°C/min.

3. Results and Discussion

3.1. Morphological Study of PBS/Nylon11 Blends

Since PBS (polyester) and nylon11 (polyamide) are condensation polymers with different functional groups, the blend has a tendency to be an immiscible blend. The addition of an epoxy-based chain extender such as Joncryl ADR-4300 having six epoxy functionalities per polymer chain, could introduce the partial-miscibility through the chain extension reaction among these polymer molecules. Figure 2 shows SEM micrographs of the PBS/nylon11 blends in various weight ratios adding 0, 0.5, and 1.0 phr of Joncryl ADR-4300. From SEM micrographs, it is clearly seen that the PBS/nylon11 blends without Joncryl ADR-4300 are an immiscible blend at which nylon11 are
dispersed phases due to the lesser weight fraction. According to MFIs by the suppliers, it should be noted that nylon11 melt is much more viscous than PBS melt under the compounding condition at 200°C. When the weight ratio of nylon11 is higher than 30 wt%, the domain size of the dispersed phases is observed to be bigger at which a domain size of >30 μm can be seen. This is attributed to the limitation of the applied shearing stress that could not transfer effectively from the PBS matrix to break the viscous nylon11 dispersed phases. Compared with the work by Lorenzo et al. [9] using the blending temperature of 210°C, the main matrix was polyamide11 at which the sizes of PBS dispersed phases increased with higher PBS content. The morphology of the PBS/nylon11 50/50 wt% blend is co-continuous that the nylon11 phases are elongated and embedded inside the PBS main matrix.

Nevertheless, there are voids between PBS matrix and nylon11 domains, which the pullout of nylon11 domains during the impact fracture is observed indicating ineffective interfacial adhesion between polymer phases if there is any. Whitening edges are observed around the empty pits implying there is stretching of the main matrix somewhat occurred before the pullout is complete. This is attributed to the possible interfacial interaction between the matrix and the dispersed phases. Due to the work by Lorenzo et al. [9], they observed there was small fibrils bonded between PBS domains and the polyamide11 matrix, but there were voids among the surface bonding. They suggested that the interaction between functional groups of polyamide11 and PBS phases. In the other words, the transesterification possibly occurred between polyamide11 and PBS phases.

Interestingly, for the PBS/nylon11 60/40 wt% blend, the domain sizes are smaller than those in the PBS/nylon11 70/30 wt% blend. This implies that the nylon11 domain sizes in this weight ratio blend are too large to be stable with the balance between surface tension and applied shear stress. Thus, they are stretched by shear stress and broken into smaller domain sizes during the melt compounding. On the other hand, the viscous nylon11 phases could form continuous phase which the PBS domains are distributed inside the matrix.

Clearly, adding Joncryl ADR-4300 into the PBS/nylon11 blends improves the compatibility among polymer molecules. This indicates by the nylon11 domains of the blends adding Joncryl ADR-4300 are smaller than the blends without this chain extender at the same weight ratio of nylon11 content. Moreover, most of the nylon11 domains embedded firmly inside the PBS matrix with just a few domains are pulled out after the impact failure. This is similarly to the work by Zhou et al. [10]. Since Joncryl ADR-4300 could initiate the chain extension reaction between PBS polyester molecules that eventually increases the molecular weight and thus increases melt viscosity of the PBS matrix as well. When the difference of melt viscosities is reduced, the dispersed phases are able to be stretched easier by the applied shear stress and thus are broken into smaller domains distributed inside the PBS main matrix.

3.2. FTIR Characterization of Neat PBS, Neat Nylon11, and the PBS/Nylon11 Blends with or Without Joncryl ADR-4300

Figure 3 presents FTIR spectra of neat PBS, neat nylon11, and Joncryl ADR-4300. For PBS polyester, the main characteristic FTIR spectra occurs at 3437.46 cm⁻¹ attributed to the O-H stretching of the PBS's end groups, at 2954.23 cm⁻¹ attributed to the C-H stretching, at 1725.27 cm⁻¹ attributed to the C=O stretching, and at 1725.27 cm⁻¹ attributed to the C-O-C stretching. For nylon11 polyamide, the main characteristic FTIR spectra occurs at 3304.36 cm⁻¹ attributed to the -NH stretching, at 2925.34 and 2854.17 cm⁻¹ attributed to the -CH stretching, at 1549.58 cm⁻¹ attributed to the -NH bending, and at 1644.21 cm⁻¹ attributed to the C=O stretching. For Joncryl ADR-4300, the wavenumbers at 1183.95, 905.93 (epoxy ring), and 757.68 cm⁻¹ are attributed to the C-O stretching, and the wavenumber at 1729.18 cm⁻¹ is attributed to the C=O stretching. The wavenumber between 3024.01 and 2954.23 cm⁻¹ is attributed to the -CH stretching. Thus, these spectra confirm that Joncryl ADR-4300 is an epoxidized ester.

For the FTIR spectra of the PBS/nylon11 blends, it is found that the FTIR spectra of the samples without Joncryl ADR-4300 were similar to those of neat PBS and neat nylon11 without any shifting. This implies that the PBS and nylon11 phases do not chemically interact to form covalent bonding between them, only having weak physical interaction via hydrophilicity of the functional groups if there is any. This correlates to the morphology of...
the blends without Joncryl in SEM micrographs that the voids between phases are present. For the blends adding Joncryl ADR-4300, the spectrum of epoxide rings could not be observed, which possibly results from only small concentration of the chain extender adding into the blends. Also, it might indicate that they had already reacted with PBS and nylon11 molecules resulting in the better compatibility of the reactive blends as evident in SEM micrographs. The chemical reaction between PBS and nylon11 via Joncryl ADR-4300 is proposed as shown in Fig. 4.

3.3. Tensile Properties of the PBS/Nylon11 Blends

Figure 5 presents Young’s modulus of neat PBS and the PBS/nylon11 blends as a function of nylon11 content. Young’s modulus of neat PBS and neat nylon11 are 242.99 ± 1.96 and 472 ± 12.70 MPa, respectively. The red line represents the rule of mixture that calculates Young’s modulus based on the modulus of neat polymer and their weight ratios as described in Eq. (2).

\[ E_{\text{blend}} = E_{\text{PBS}}w_{\text{PBS}} + E_{\text{nylon11}}w_{\text{nylon11}} \]  

(2)

It was seen that Young’s modulus of mostly blends without Joncryl ADR-4300 was following the rule of mixture. However, the PBS/nylon11 60/40 wt% blend had higher Young’s modulus than the calculated value. Since the domain sizes of the PBS/nylon11 60/40 wt% were smaller than that of the PBS/nylon11 70/30 wt% under the same mixing condition, the smaller dispersed phases of nylon11 with higher content became the reinforcing fillers in the PBS matrix. Since the interfacial interaction between the PBS matrix and the nylon11 dispersed phases is observed in SEM micrograph, the load transfer from the softer main matrix to the more rigid dispersed phases could be achieved. However, adding Joncryl ADR-4300 as a chain extender did not increase the rigidity of the blends although the better compatibility between phases was introduced which the finer dispersed phases embedded inside the PBS matrix with less voids.
Figure 6 and 7 present tensile strength and elongation at break of neat PBS and the PBS/nylon11 blends as a function of nylon11 content, respectively. Similarly, the rule of mixture was applied and the red line represented the values of tensile strength of the blends that followed the rule. Clearly, the tensile strength of the blends was lower than the calculated values. This emphasized the incompatibility between PBS and nylon11 phases. Incorporating Joncryl ADR-4300 into the PBS/nylon11 blends increased the values of the tensile strength attributed to the limited improvement of interfacial interaction between phases. As seen in SEM micrographs, the dispersed phase size of nylon11 was reduced and embedded inside the PBS matrix. This caused the tensile strength to be higher compared to the blends without the chain extender. Nevertheless, the improvement was considered to be limited, since the tensile strength value was still lower than those of both neat PBS and neat nylon11, and elongation at break was much lower than neat polymers. This was due to the possibility of chain scission of PBS molecules caused by the chain extension reaction. Although the reaction did improve the interfacial interaction between phases, the pullout of the dispersed phases in the blends with nylon11 content lower than 30 wt% were still observed.

It was found that the trend of elongation at break was lower for the PBS/nylon11 blends adding 30 wt% nylon with Joncryl ADR-4300. From SEM micrographs, the dispersed phases of nylon11 at the weight ratio of 30 wt% without Joncryl ADR-4300 were the largest due to agglomeration. The size of dispersed phase was reduced significantly after incorporating with Joncryl-4300, and the interfacial adhesion was improved as evident in the increase of tensile strength. Although these dispersed phases were smaller, they were still agglomeration-alike compared to the other compositions. Those agglomerated sites became the stress concentrators that the matrix and the dispersed phases were separated due to the higher non-uniform distribution of the domain size.

3.4. Impact Strength of the PBS/Nylon11 Blends

Figure 8 presents impact strength of neat PBS and the PBS/nylon11 blends plotting as a function of nylon11 content. In this study, the neat PBS specimen had an impact strength of 10.16 ± 3.4 kJ/m² while the neat nylon11 had an impact strength of 10.67 ± 0.34 kJ/m². Since the values of impact strength of these polymers were closed in values, the impact strength of the blends theoretically would not be different from the neat polymers as shown in the rule of mixture (red line). However, the massive reduction of impact strength was observed when the blends consisted of nylon11 less than 20 wt%. In addition, adding Joncryl ADR-4300 into the blends in these weight ratios did not improve the impact strength of the blends. This results emphasized effect of stress concentration introduced by those small dispersed phases of nylon11 that allowed crack propagation to occur in the blends easier compared to neat polymer. When the nylon11 content was 30 wt%, the blend had significant improvement of impact strength. This related to the PBS matrix shrink around these nylon11 domains and generated high physically interfacial adhesion that higher energy was required to break them apart or even pull-out these domains from the main matrix. This was similarly to the work by Moriyama et al. [4], which they explained that a larger shrinkage ratio difference between polyamide11 and PBS formed a larger dilational stress field resulting in a higher impact strength. When adding Joncryl, this effect was less dominant due to smaller domain sizes, so that the impact strength was reduced to be in the same range of those of neat polymers.

3.5. Thermal Property Analysis of Neat PBS and PBS/Nylon11 Blends by DSC

Table 2 presents glass transition temperatures (Tg), crystallinity temperatures (Tc), crystal melting temperatures (Tm), and the degree of crystallinity (Xc). Figures 9 and 10 show crystallization temperatures of PBS and nylon11 phases, and the degree of crystallinity of PBS and nylon11, respectively. Neat PBS showed Tg at -32.5°C which it was not shifted significantly when melt blending with nylon11 with or without the chain extender. It was expected that the Tg would be shifted when the chain extension reaction took place resulting on the linking among molecules or the reduction of molecular weights occurred to allow better
mobility of short-chain molecules. Moreover, the $T_m$ of both polymers showed at the same temperatures of those neat polymers, which indicated there was no presence of the transesterification as reported by Sang-Woo Kim [11]. Nevertheless, the $T_m$ of PBS phase was shifted to higher temperature when blending with nylon11. This implied that nylon11 dispersed phases that crystallized first at about 163°C acted as the nucleating agents for the PBS molecules to crystallize. The percentage of crystallinity did not differentiate significantly when the nylon11 content was varied. Since the $T_m$ of PBS was still the single peak, this implied the crystal form was similar compared to neat PBS.

Table 2. Glass transition temperatures ($T_g$), crystallization temperatures ($T_c$), crystal melting temperatures ($T_m$), and the degree of crystallinity ($X_c$).

| Sample          | $T_{gPBS}$ (°C) | $T_{gcnylon11}$ (°C) | $T_{mPBS}$ (°C) | $T_{mcnylon11}$ (°C) | $T_g$ (°C) | $T_m$ (°C) | $X_c$PBS (%) | $X_c$nylon11 (%) |
|-----------------|-----------------|----------------------|-----------------|----------------------|-----------|-----------|--------------|----------------|
| Nylon11         | n/a             | 59.48                | n/a             | 184.95               | -         | 162.51     | n/a          | 21.66          |
| PBS             | -32.52          | n/a                  | 113.23          | n/a                  | 76.04     | -         | 53.63        | n/a            |
| P9N1            | -32.45          | 59.25                | 113.48          | 183.35               | 84.35     | 165.64     | 48.41        | 16.80          |
| P8N2            | -32.41          | 59.08                | 113.44          | 183.04               | 84.22     | 165.30     | 49.04        | 16.14          |
| P7N3            | -32.03          | 58.69                | 113.97          | 184.57               | 83.21     | 164.03     | 24.26        | 6.18           |
| P6N4            | -31.88          | 59.44                | 115.98          | 185.38               | 82.36     | 163.38     | 24.99        | 6.25           |
| P5N5            | -32.46          | 61.11                | 114.93          | 184.63               | 82.61     | 163.36     | 44.44        | 14.62          |
| P9N1_0.5 phr    | -32.48          | 59.35                | 113.43          | 183.21               | 82.27     | 164.75     | 49.94        | 22.09          |
| P8N2_0.5 phr    | -32.59          | 59.32                | 112.91          | 182.86               | 81.68     | 165.48     | 54.53        | 15.68          |
| P7N3_0.5 phr    | -32.27          | 59.58                | 113.71          | 183.86               | 79.93     | 163.49     | 46.89        | 16.62          |
| P6N4_0.5 phr    | -32.40          | 59.92                | 115.39          | 184.30               | 79.90     | 163.18     | 49.95        | 19.67          |
| P5N5_0.5phr     | -32.43          | 59.46                | 114.55          | 184.08               | 80.12     | 163.06     | 52.22        | 21.03          |
| P9N1_1phr       | -32.22          | 59.35                | 113.19          | 183.29               | 79.05     | 164.57     | 45.75        | 14.13          |
| P8N2_1phr       | -32.19          | 59.29                | 111.97          | 182.51               | 75.47     | 163.30     | 47.17        | 16.33          |
| P7N3_1phr       | -37.68          | 59.62                | 114.74          | 184.84               | 77.41     | 163.42     | 32.38        | 11.02          |
| P6N4_1phr       | -32.65          | 57.16                | 115.11          | 184.20               | 80.54     | 163.48     | 43.28        | 13.20          |
| P5N5_1phr       | -32.30          | 59.66                | 113.55          | 183.29               | 80.26     | 163.54     | 52.58        | 18.98          |

Fig. 9. Crystallization temperatures of PBS and nylon11 phases with and without Joncryl ADR-4300.

Fig. 10. Degree of crystallinity ($X_c$) of PBS and nylon11 phases in the blends with and without Joncryl ADR-4300.
Table 3 presents thermal degradation temperatures (T_d) of neat PBS and PBS/nylon11 blends, which Figure 11 compares the first and the second derivative (DTG) curves of these materials as a function of nylon11 content. It was seen that neat PBS and neat nylon11 showed only one-step thermal degradation with the T_d at 345.9°C and 412.7°C, respectively. For the PBS/nylon11 blends, there were two thermal degradation steps that correlated to the thermal degradation of PBS and nylon11 separately. For melt blending without Joncryl ADR-4100, it was found that the T_d,PBS was reduced with the increase of nylon11 content. The reduction of T_d,PBS implied the decrease of PBS molecular weight during the melt blending with nylon11.

![Figure 11. Degradation temperatures of neat PBS and the PBS/nylon11 blends under nitrogen atmosphere.](image)

Fig. 11. Degradation temperatures of neat PBS and the PBS/nylon11 blends with and without Joncryl ADR-4300.

The thermal degradation of PBS was discussed extensively in the work by Rizzarelli et al. [12]. Thermo-oxidation process causes a significant reduction of the molecular weight of the polyesters, promoting the formation of PBS oligomers with different end groups. These newly formed end groups with hydroxyl or carboxylic acid end groups could interact with the adjacent molecules as known as the transesterification reaction. When Joncryl of 0.5 wt% was added into the melt blending, the T_d,PBS increased with the PBS content of 10-20 wt%, and then sharply dropped with the nylon11 content of 30-50 wt%. This confirmed the role of Joncryl ADR-4300 to initiate the chain extension reaction with PBS or nylon11 molecules. The chemical reaction scheme between epoxide groups of Joncryl ADR-4300 and hydroxyl end groups in the PBS or nylon11 molecules is proposed as shown in Fig. 12. When the epoxide groups of Joncryl ADR-4300 reacted with the hydroxyl or the carboxylic end groups between two PBS molecules, it extended the molecular chains of PBS. In contrast, when the epoxide groups reacted with the amide groups in PBS polymers, the PBS molecules would also be broken into two fragments causing the reduction of molecular weights.

![Figure 12. The chemical reaction scheme between epoxide groups of Joncryl ADR-4300 and hydroxyl end groups of PBS or nylon11 molecules.](image)

Fig. 12. The chemical reaction scheme between epoxide groups of Joncryl ADR-4300 and hydroxyl end groups of PBS or nylon11 molecules.
4. Conclusion

The morphology of PBS/nylon11 blends indicated that they were immiscible blends which it was a sea-island structure when polyamide11 less than 50 wt%. Adding Joncryl ADR-4300 introduced better chemical compatibility in the blends evident by smaller dispersed domain sizes and less pullout. The blends with higher polyamide11 content had greater Young’s modulus following the rule of mixture, however, the rigidity was reduced when adding the chain extender. The impact strength of the blends with polyamide11 content higher than 30 wt% was enhanced significantly with the presence of chain extender, although tensile strength and elongation at break were reduced. The crystallization temperature of PBS increased with higher polyamide11 content due to the nucleation effect, although the degree of crystallinity was in the same range. The thermal degradation temperature of the blend was shifted to higher temperature confirming the chain extension reaction occurred.

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