

Impact Strength and Morphology of Sustainably Sourced Recycling Polyethylene Terephthalate Blends

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Polyethylene terephthalate (PET) is a semi-crystalline material that is widely used in the packaging industry, mainly in the production of bottles for beverages. Similar to other plastics, PET causes a problem in disposal as it remains in the environment for a long time. Most of the bottles are thrown away after a single usage, which worsens the disposal problem. Recycling is one of the best ways to reduce the problem of disposal. However, recycling reduces the mechanical and chemical properties of the PET. Factors such as moisture absorption, biological pollutants, oxidation, high temperature, and thermal degradation have reduced the molecular weight of PET. To improve the properties, recycled PET had been blended with Polyamide 11 (PA11) at different ratios of PET: PA11, 30:70, 50:50, and 70:30. A modified styrene/acrylic/epoxy chain extender (Joncryl) was added at 1 wt % in the blend to enhance the properties. The properties of recycled PET/PA11 blends were investigated in terms of mechanical and morphological aspects. The impact strength of recycled PET/PA11 blend at the ratio of 30/70 had recorded the highest impact strength of 54.67 J/m, owing to the good impact property of PA11. The addition of 1 wt % modified styrene-acrylic chain extender (Joncryl) had further enhanced the impact strength of the blends. The findings were supported by the morphologies analyses that showed the existence of the co-continues phases and less pull out effect of particles with the addition of Joncryl. Recycled PET/PA11 blends have potentials to be used in various applications that related to the structural application of automotive and construction.

1. Introduction

Sustainable blending involving petroleum-based and biodegradable or bio-based polymers has drawn a great concern on the environmental problems caused by synthetic materials. This is because synthetic polymers can be seen everywhere from household applications to industrial products. However, the wastes produced by these materials are increasing continuously which harms the environment due to their slow degradation and non-biodegradable properties. The number of plastic wastes entering the ocean from the land was estimated between 4.8 and 12.7 Mt globally in 2010 (Okan et al., 2019). This shows that plastic wastes are one of the major components that negatively affecting aquatic life. One of the plastic wastes that concern environmental health is polyethylene terephthalate (PET). PET is a semi-crystalline polymer derived from ethylene glycol and terephthalic acid. PET imparts a notable strength and stiffness, due to the large aromatic ring in the repeating units, especially when the polymer chains are aligned with each other upon drawing or stretching. In the commercial industry of food packaging, bottles made from PET are one of the most preferred containers due to the nontoxicity, strength, transparency, lightweight, resealability, shatter resistance, and recyclability (Dasan, 2015). In the sector of food packaging, PET is the standard plastic with the highest consumption (Casazza et al., 2019).

Despite all the good properties owned by PET, the properties decrease after being recycled. This is because, during the process of recycling, the molecular structure of PET is broken down into shorter chains, by thermal degradation, which reduces the molecular weight and weakens the PET compared to the original state (Gere and Czigany, 2020). The breaking of the chains are also influenced by the moisture absorption, biological contamination, oxidation and high temperature which adversely affect the mechanical properties of PET such as becoming more brittle and losing its melting elasticity (Khoramejadian and Branch, 2014).

One of the methods used to regain the properties of recycled PET is by blending with other tough polymeric materials. Blending is a convenient alternative for the development of polymeric materials which gives benefits such as processing simplicity and cost-effective compared to other alternatives. To use the recycled PET in high-performance applications, blending the recycled PET with other polymers is a promising alternative.

One of the possible materials is polyamide 11 (PA11). PA11 is a semi-crystalline material that is produced from a renewable resource castor oil (Mancic et al., 2015). PA11 is an interesting commercial aliphatic polyamide that exhibits excellent characteristics such as good oil resistance, and less hydrophilic as compared to the commonly used polyamide-6 and polyamide-6,6 (Sahnoune et al., 2017). Using a bio-based material like PA11 will help to reduce the environmental problem.

Aside from blending with PA11, the addition of a chain extender in the formulation can also contribute a positive impact on the properties of the recycled PET. Chain extender extends or forms branches with the short chains of recycled PET which increases the molecular weight consequently improves the melt strength of the recycled PET (Nofar and Oğuz, 2019). Many commercially available chain extenders are available for recycled PET including organic phosphates (Diani and Gall, 2006) and oligomeric polyisocyanates (Zhang et al., 2009). The nature, reactivity and number of functional groups on the chain extender molecules determine the properties of the final product. In this study, recycled PET was blended with PA11 at different PET: PA11 ratios, using an internal mixer. A modified styrene/acrylic/epoxy chain extender (brand name Joncryl) was incorporated into the blend at fixed 1.0 wt %. Joncryl was selected because it contains a reactive glycidyl methacrylate group that can react with both reactive functional end chains of PET (hydroxyl and carboxyl groups) and PA11 (amine and carboxyl groups). Previous study showed that Joncryl had imparted dual actions i.e. as chain extender and compatibiliser to the polymeric systems (Nofar and Oğuz, 2019). The effects of PET/PA11 ratio (with and without Joncryl) on the impact and morphological properties of the blends were investigated and discussed.

2. Materials and methods

2.1 Materials

The materials used to prepare the PET/PA11 blends were an amorphous recycled polyethylene terephthalate (PET), a semi-crystalline polyamide 11 (PA11), and a modified styrene/acrylic/epoxy chain extender. The amorphous recycled PET from a post-industrial waste was obtained from ALBA Polyester Sdn Bhd (Johor, Malaysia), PA11 was purchased from Arkema (Rilsan®) and modified styrene/acrylic/epoxy chain extender (Joncryl ADR-4368-C, Mw of 6800 g/mol, an epoxy equivalent weight of 285 g/mol, epoxide functionality of 9). The chemical structure of PET, PA11 and Joncryl was depicted in Figure 1. Joncryl was used as a chain extender and compatibiliser in this work.

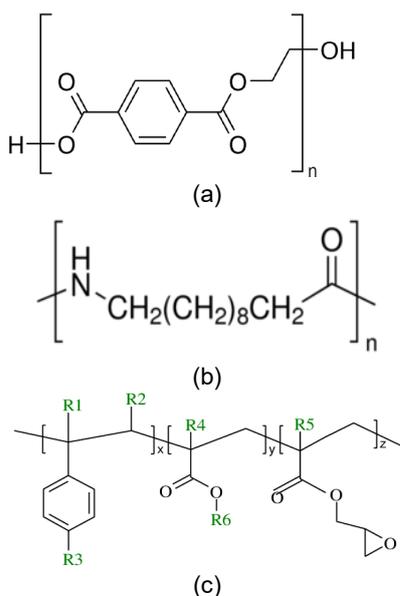


Figure 1: Chemical structure of (a) PET; (b) PA11; (c) Joncryl ADR-4368-C. R1 – R5 is H, a higher alkyl group or the combination; R6 is an alkyl group; x, y and z are repeating units between 1 and 20.

2.2 Blend preparation

Recycled PET pellet, PA11 pellet and Joncryl powder were dried at 60 °C overnight before the blending process. A Brabender GmbH and Co. KG with a rotor speed of 60 rpm, processing temperature of 250 °C and a mixing time of 6 min was used for mixing purpose. The blends were prepared in two different batches; recycled PET/PA11 without Joncryl (R series) and recycled PET/PA11 with 1.0 wt % Joncryl (J series). The amount of 1 wt % Joncryl was following the manufacturer's recommendation for rigid PU foam (BASF, 2006). The formulations of all blends were listed in Table 1.

Table 1: Composition of PET/PA11 blends at different ratios

| Description | Sample Code | Recycled PET | PA11 | Joncryl (wt %) |
|--------------------------------|-------------|--------------|------|----------------|
| Neat recycled PET | R100/0 | 100 | | 0 |
| Recycled PET/PA11 | R70/30 | 70 | 30 | 0 |
| | R50/50 | 50 | 50 | 0 |
| | R30/70 | 30 | 70 | 0 |
| Neat PA11 | R0/100 | | 100 | 0 |
| Neat recycled PET with Joncryl | J100/0 | 100 | | 1.0 |
| Recycled PET/PA11 with Joncryl | J70/30 | 70 | 30 | 1.0 |
| | J50/50 | 50 | 50 | 1.0 |
| | J30/70 | 30 | 70 | 1.0 |
| Neat PA11 with Joncryl | J0/100 | | 100 | 1.0 |

2.3 Mechanical analysis

The impact strength was determined with the Izod impact test on an Izod impact tester. The measurements were performed according to ASTM D256, where the dimension of the specimen was set at 125 mm length with a cross-section of 3.2 mm x 12.7 mm and 3 mm notched. The test was carried out at room temperature and the average of five specimens for each composition was calculated. The flexural test was carried out according with ASTM D790.

2.4 Morphological analysis

Scanning electron microscopy (SEM) was used to analyse the morphology of the recycle PET/PA11 blends. Fractured samples from the impact test were analysed using an acceleration voltage of 10 kV and 7000X magnification. All specimens were coated with a thin film of gold to prevent the electron charges from damaging the samples.

3. Results and discussion

3.1 Impact test

The mechanical properties of recycled PET/PA11 blends were shown in Table 2. It can be seen that the impact strength increased with increasing PA11 ratios for both R (without Joncryl) and J (with Joncryl) series. The addition of 1 wt % of Joncryl into the blend had increased the impact strength of the blends, neat recycled PET and PA11 resins. Joncryl had chain-extended both end groups of PET and PA11, increasing the molecular weight of the samples, and improved the mechanical properties. The impact strength of neat recycled PET was failed to be measured due to its high brittleness. This might be due to the degradation of the recycled PET chain via hydrolysis during processing, which shortens the recycled PET chain and increased the brittleness of the neat recycled PET samples. Upon the addition of Joncryl, the impact strength was recorded at 21.85 J/m, which showed an improvement with respect to the recycled PET chain without Joncryl. As shown in Figure 1, the glycidyl methacrylate group in Joncryl can interact with the hydroxyl and carbonyl groups in recycled PET and reduces the degradation of the recycled PET chain. As reported by Tavares et al. (2016), the molar mass of PET was increased with the addition of Joncryl, corresponding to the chain extension reaction.

The impact strength was slightly increased for both R-series and J-series when 30 wt % and 50 wt % of PA11 were added into the recycled PET, due to the toughening effect brought by PA11. The slight reduction was observed in impact strength for J-series at 70/30 blend ratio. This probably due to poor interfacial interaction between the particles of PA11 and the recycled PET matrix. The addition of Joncryl did not give a great effect on the phase interaction between the polymers, because PET was still the dominant phase of the blend. This argument was supported by the morphology analysis of SEM (Figures 3a and 3b), where the pullout of PA11

particles was seen from the images. When the blend ratio was increased to 50/50 PET/PA11, the impact strength for both series were also increased, where J series (35.29 J/m) had a slightly higher value than that of R-series (32.60 J/m). In the J-series, Joncryl had formed the chain extension with both phases, resulting in a well-blended and no obvious phase separation morphology that contributed to the increment in impact strength.

When the blends ratio was changed to 30/70 PET/PA11, the impact values were drastically increased for both J- and R-series, reflecting the great influence of PA11 on the impact strength. In the presence of Joncryl, the J series experienced a nearly two-fold increase of the impact strength (98.91 J/m) when compared the R-series (54.67 J/m). It was thought that Joncryl had a better interaction with PA11 because of the reactivity of the end groups. The epoxide group of Joncryl was favoured to react with the amine group of PA11 when compared to the hydroxyl and carboxyl groups of PET. The arguments on 'reactivity favouritism of Joncryl' was clearly proven at 0/100 ratio of PET/PA11 where the impact strength of J-series (444.47 J/m) had increased at about 72 % with respect to the R-series (258.57 J/m). By increasing the PA11 ratio has directly increased the number of amine groups available for the chain extension and positively affected the impact properties of the blend. The findings were compliance with the morphology analysis of 30/70 blends where smaller dispersed phase and less particle pullout were observed through the images (Figure 3f).

The toughing properties are further supported by the flexural test data. Figure 2 shows the flexural strength of the blends for R and J series. From this data, the flexural strength reduces for J series which indicate that the flexibility of recycled PET/PA11 blends improved with the addition of Joncryl.

Table 2: Impact strength of recycled PET/PA11 blends

| Samples (recycled PET/PA11) | Impact strength (J/m)-R series | Impact strength (J/m)-J series |
|--------------------------------|-----------------------------------|-----------------------------------|
| 100/0 | ** | 21.85 |
| 70/30 | 23.65 | 22.70 |
| 50/50 | 32.60 | 35.29 |
| 30/70 | 54.67 | 98.91 |
| 0/100 | 258.57 | 444.47 |

** No values since the samples are not able to be prepared due to the excessive brittleness.

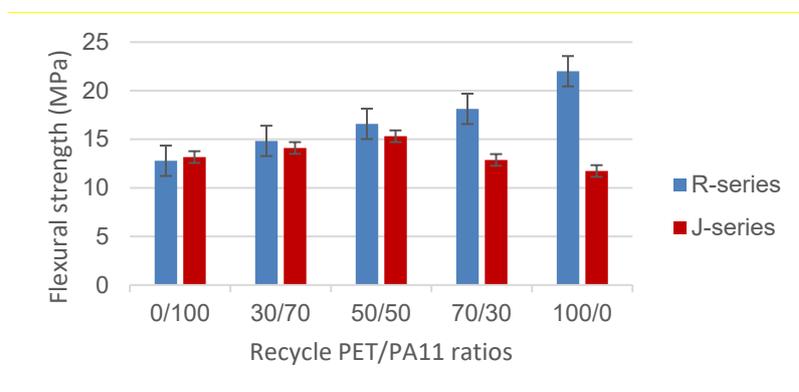


Figure 2: Flexural strength of R and J series of recycled PET/PA11 blends

3.2 Morphological properties

SEM micrographs of recycled PET/PA11 blends with and without Joncryl at different compositions were presented in Figures 3a to 3f. As can be seen in Figure 3a, the morphology of the dispersed PA11 particles in the continuous recycled PET matrix was formed at 70 wt % recycled PET. The addition of Joncryl (Figure 3d), has caused an increase in PA11 particle size and more particles pullout were observed which negatively affected the impact property. When the ratio was set at 50/50 PET/PA11, both R-series and J-series formed the morphologies where no obvious phase separation was seen (Figures 3b and 3e). The J-series showed a well-blended smooth phase with no void or phase pulls out effect, manifesting to the increase of the impact strength as discussed in Section 3.1. Different morphologies were observed for the blends with 30/70 PET/PA11 (Figures 3c and 3f), where the recycled PET particles were dispersed in the PA11 matrix. The size of the dispersed recycled PET particles were smaller than the size of the dispersed PA11 particles in 70/30

blend ratios (Figures 3a and 3d). For the J-series, the addition of Joncryl had improved the chain interaction between the phases where fewer particles pull out (PET particles) from the PA11 matrix were observed. This was thought due to the good molecular interaction and better interfacial adhesion between both phases since Joncryl can also act as a compatibilizer that reduces the interfacial tension of polyesters. Nofar and Oğuz (2019) had reported on the ability of Joncryl to reduce the interfacial tension between polyester polylactic acid and PA11 blends.

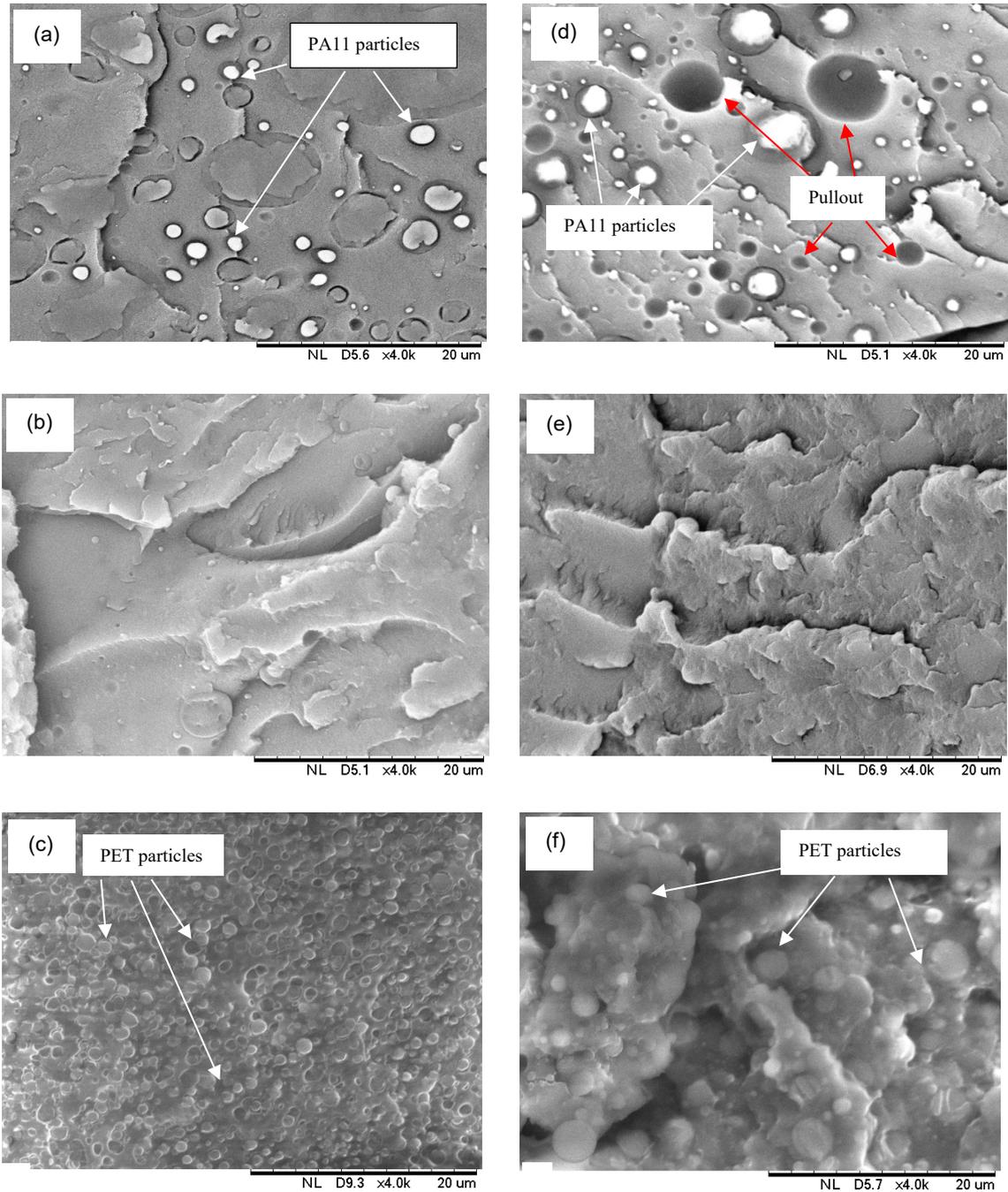


Figure 3: SEM micrographs of recycled PET/PA11 with (a) R70/30; (b) R50/50; (c) R30/70; (d) J70/30; (e) J50/50; and (f) J30/70.

4. Conclusions

Recycled PET and PA11 blends were successfully prepared and the effect of blend ratio and Joncryl addition on the impact properties and morphology of recycled PET/PA11 blends was successfully investigated. It was found that PA11 had a dominant effect on the impact strength of the blends for both R-series and J-series. The addition of modified styrene/acrylic/epoxy chain extender (Joncryl) into the blends had a great influence on the impact strength for all ratios as well as the neat materials. Sample J-series with 100 wt % PA11 had higher impact strength (about 72 %) than the sample of R-series with 100 % PA11. This was due to the reactivity of the end groups of the components where the epoxide group of Joncryl was favoured to react with the amine group of PA11 rather than the hydroxyl and carboxyl groups of PET. The SEM analysis showed that the morphologies of the blends had changed according to the ratio of PET/PA11 and the addition of Joncryl. When PET was a dominant phase (70 wt %), the pull out effect of PA11 was seen from the images, indicating poor interfacial interaction between the phases. When the ratio was equal (50 wt %), the co-continuous phase existed within the blend. At the higher PA11 ratio, the morphology analysis revealed that both R-and J-series were immiscible. It can be concluded that PA11 was effective to be blended with the recycled PET to enhance the toughness of the recycled PET. A small amount of Joncryl at 1 wt % was adequate to impart toughness into the blend materials. With these findings, the recycled PET/PA11 blend has potentials to be used in the wide area of applications such as structural applications in automotive and construction.

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