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Research paper

The Effect of MAPP Compatibilizing Agent on the Mechanical and Thermal Properties of Polypropylene/PLA Blends

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Abstract

In this study, the polymer blends were prepared in the ratios of Polypropylene (PP) to Polylactic acid (PLA) of 70:30 by weight. Maleic anhydride-grafted polypropylene (MAPP) was used as a coupling agent to improve the compatibility between PP and PLA. The MAPP was added into the blend in the ratio of 0, 3, 6 and 9% wt. The polymer blends were prepared by extrusion process using twin screw extruder. The effects of MAPP content on the mechanical and thermal properties of PP/PLA blend were investigated. The result of tensile strength shows no significant increased with the addition of MAPP content. However, Young modulus and Izod impact strength shows significantly increased with the addition of MAPP content. Tensile modulus increased up to 43% with the addition of 6% wt. MAPP. TGA results show that blending PP with PLA cause increased the thermal stability of PLA. The incorporation of 6 % MAPP has shifted the initial weight loss of PP component towards lower temperature.

Keywords: *Coupling Agent, Extrusion, Mechanical Properties, Polylactic Acid, Polymer Blends,*

1. Introduction

Polypropylene (PP) is one of the most versatile thermoplastic polymers and widely used in the disposable products such as food packaging and household equipment due to its low in cost, high thermal stability and low density. The drawn back of this material is, it is not biodegradable. Recently, PLA (Polylactic acid) has been used as an important bio-based polymer in the biomedical and environmental products since its merit of bio-degradability, bio-compatibility, and non-toxicity [1-2]. Blending of synthetic polymer such as PP and PE (polyethylene) with biodegradable polymer such as PLA can reduce the environmental problem. Biodegradable polymers will induce gradual decomposition of conventional polymers. This phenomenon is named as bio disintegration. However, blending of non polar polymer such PP with polar PLA usually faces incompatibility of the polymers blends and causes reduction in its thermal and mechanical properties [2]. Therefore, in order to enhance the mechanical properties of polymer blends the compatibilizing agents were used to provide miscibility between neat polymers through reduction of the interfacial tension. Studies show that, incorporation of compatibilizers such as maleated polyethylene (MAPE) and maleated polypropylene (MAPP) or carboxylated PE played an important role in improving the miscibility and bonding strength between hydrophilic fillers and hydrophobic thermoplastics such as PP or PE [3-4]. Nalin et al (2014) [5] observed that 3 wt.% PP-g-MA compatibilizer gave an increased in thermal stability of PP and PLA blends prepared at different weigth ratios. Study by Xiangdong et al. (2014) on the effect of MAPP at various composition on PLA/MAPP blend found that, MA reacted with PLA, and thus a small amount of branched polymer was formed [6]. The formation of this branched polymer attributed to the reaction between MA groups and hydroxyl groups on the PLA chains. Therefore, this branched polymer could reduce the interfacial tension due to its good compatibility with both PLA and PP.

In our study, different weight ratios of compatibilizing agents Maleic anhydride-grafted polypropylene (MAPP) were used to investigate their effect on the mechanical, morphological and thermal properties of PP/PLA blend prepared in the ratio of PP to PLA : 70/30 by weight %. All the materials was melt-blended in the twin screw extruder.

2. Experiment

2.1. Materials

Polypropylene (PP) used in this study was produced by Petronas Chemical Polypropylene Sdn. Bhd. with density of 0.95g/cm^3. Polylactic acid (PLA) was produced by Nature Works LLC and compatibilizer used was commercial Maleic anhydride-grafted polypropylene (MAPP), purchased from Sigma-Aldrich Malaysia.

2.2. Preparation of Polymer Blending

The mixing of PP and PLA with compatibilizer was melt-blended in the twin screw extruder in the ratios of PP to PLA of 70:30 by weight. All materials were dried at 80^{0}C for 12 hours to avoid moisture. The temperature and screw speed of the extruder was set at 195 ^{0}C, 200 ^{0}C, 195 ^{0}C, 190 ^{0}C and 60 rpm, respectively. The MAPP compatibilizer content was varied from 0, 3, 6 and 9 wt.% of polymer blends as shown in Table 1. The extrudate was subsequently cut into pallet prior to compression and injection moulding process.

Table 1: Material formulations in the blends preparation

Samples	PP (wt.%)	PLA (wt.%)	MAPP (wt.%)
PP	100	0	0
PP/PLA	70	30	0
PP/PLA-3 % MAPP	70	30	3
PP/PLA-6 % MAPP	70	30	6
PP/PLA-9 % MAPP	70	30	9

The prepared batch was then hot pressed at a temperature of 200^0C for 7 minutes followed by cold press for 5 minutes under the same pressure to obtain 3 mm thick specimens for Izod impact test.

2.3. Mechanical Testing and Characterizations

The Izod impact test was studied according to ASTM D 256 using a Ray Ran Izod impact testing machine with 5.5 Joule hammer. About ten specimens were used for this testing.

Tensile test specimens were prepared using Thermo Haake Mini Jet injection molding machine. Tensile measurement was conducted based on the ASTM D638 using a Testometric 500, tensile testing machine with the cross-head speed of 50 mm/min. At least five specimens of each composition were tested for the tensile measurements and the average values were recorded.

The morphology of polymer blends was examined by scanning electron microscope (SEM) using Hitachi TM3030Plus SEM at an acceleration voltage of 15 kV to evaluate the possible differences in fracture surfaces. Samples for morphological analysis were observed from tensile test specimens. The tensile fractured surfaces were coated with gold to avoid charging under the electron beam.

Thermogravimetric Analysis (TGA) was carried out using Netzsch TG209 TGA analyzer. The sample was scanned from temperature of 30 to 600°C at a heating rate of 10°C/min.

Fourier Transform Infrared (FTIR) spectroscopic measurements of PP/PLA with and without MAPP blends were obtained using a FTIR spectrometer (Bruker TENSOR 27). The sample used was in the form of film. Each spectrum was obtained within the range of 4000 – 400 cm^{-1}.

3. Results and Discussion

3.1. Tensile and Izod Impact Test

The effect of MAPP compatibilizer on mechanical properties of PP/PLA blends were investigated using tensile and Izod impact test. The results are shown in Table 2. Generally, the result shows that both the tensile strength and Young's modulus increased by incorporating 3 to 6 wt% MAPP into PP/PLA blend. The addition of 30 wt.%. PLA into the blend had increased the tensile strength up to 30% as compared to neat PP. However the incorporation of MAPP into the PP/PLA blend shows slightly increased in tensile strength (7%). It is worthwhile to note, that tensile strength enhancement even if small (Figure 1), is an indicator of a good compatibility between PP and PLA. This increase in tensile strength of the PP/PLA blend is probably because that the MAPP may only exist at the boundary of the PP and PLA and act as a connector to hold domains, and consequently results higher mechanical strength [7]. However, the tensile strength of the PP/PLA blends decreases with the increase of MAPP content up to 9 wt.%.

The result shows, Young's modulus of pristine PP was about 1325.6 MPa and the corresponding value for PP/PLA:(70/30) blend slightly increased to 1327.3 MPa. Meanwhile, incorporation of 3 wt.% MAPP has significantly increased the Young's modulus of PP/PLA blend to 1547.3 MPa. The main cause was the compatibilized effect of MAPP. The highest value attained was 2032.4 MPa which is up to 53% increment in comparison to neat PP/PLA blend as 9 wt% MAPP was added into the polymer blend.

On the other hand, the presence of 9 wt% MAPP shows a negative effect on the tensile strength result. Thus it is worthwhile to note, that for higher amount of compatibilizer the expected tensile strength improvement related to the better PP-PLA compatibility is not occurring and therefore an optimal compatibilizer concentration can be detected at 3 to 6 wt%.

Table 2: The results of tensile and Izod impact test

Sample	Tensile Strength (MPa)	Young's Modulus (MPa)	Strain at Break (%)	Impact Strength (kJ/m^2)
PP	30.11	1325.60	30.05	2.32
PP/PLA	39.21	1327.33	16.60	1.77
PP/PLA-3 % MAPP	42.11	1547.28	10.73	1.81
PP/PLA-6 % MAPP	42.90	1906.39	10.96	1.23
PP/PLA-9 % MAPP	37.94	2032.37	10.36	1.24

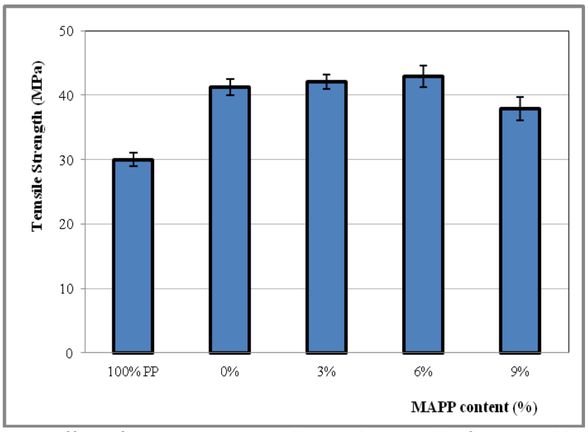

Fig. 1: Effect of MAPP content on the tensile strength of PP/PLA blend

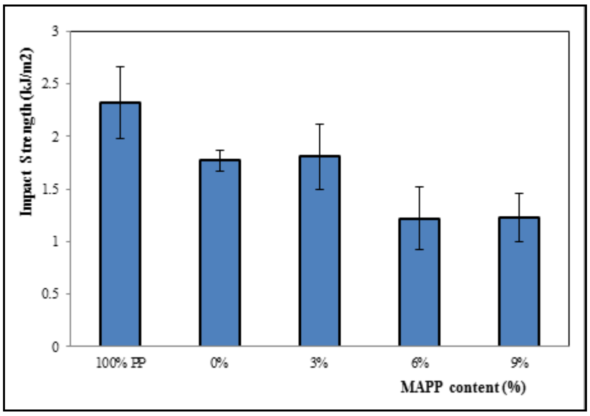

Fig. 2: Effect of MAPP content on the impact strength of PP/PLA blend

Figure 2 shows the results of Izod impact strengths of PP/PLA blends added with different amount MAPP loadings. In contrast with tensile strength result, the impact strength of neat PP higher than that of PP/PLA polymer blend with and without MAPP compatibilizer. The decreasing in impact strength was significant for the PP/PLA blend as compare to neat PP, which suggested that PLA cause the blend became brittle. The addition of MAPP compatibilizer into the polymer blends did not give significant changes in the impact strength properties of PP/PLA blend.

3.2. Thermal stability

The TGA is a technique that measures the change in mass of the sample during heating as a function of temperature. Figure 3 shows TGA curve of neat PLA, PP, PP/PLA blend and PP/PLA with 6 wt% MAPP. The evaluation of the thermograme is presented in Table 3. During thermal degradation, the TGA curves displayed a single step degradation process for neat PLA and PP. As shown in Figure 3, PP was thermally more stable than PLA. The onset temperature (T_{onset}) of thermal degradation of PLA was 305 ^oC, whereas PP started to degrade at 442 ^oC and completed at 483 ^oC. The TGA curves for blends showed the two degradation transitions. The percentage weight loss in the first and second decomposition step related to the amount of PLA (30 wt.%) and PP (70 wt.%). It also shows that blending PP with PLA cause increased the thermal stability of PLA, but not the thermal stability of PP.

The incorporation of 70 wt % PP in the blend resulted in the increase of T_{onset} of PLA from 305 ^oC to 336 ^oC. Somehow, the temperature maximum (T_{max}) almost the same in the case of the blend (357 ^oC), as compared with that of the neat polymer (368 ^oC). Conversely the result shows that, the presence of 6 % MAPP has shifted the initial weight loss of PP component towards lower temperature, it led to decrease in T_{onset} of PP from 444 ^oC to 423 ^oC.

It can be also seen that the effect of MAPP is more pronounced on the PP than PLA. This indicated the absence of any reaction taking place within the blend constituents. This trend also reported by Teli & Desai [8]. Thus, blending of 70 wt% PP with 30 wt% PLA with and without MAPP resulted in no enhancement in the thermal stability of PP.

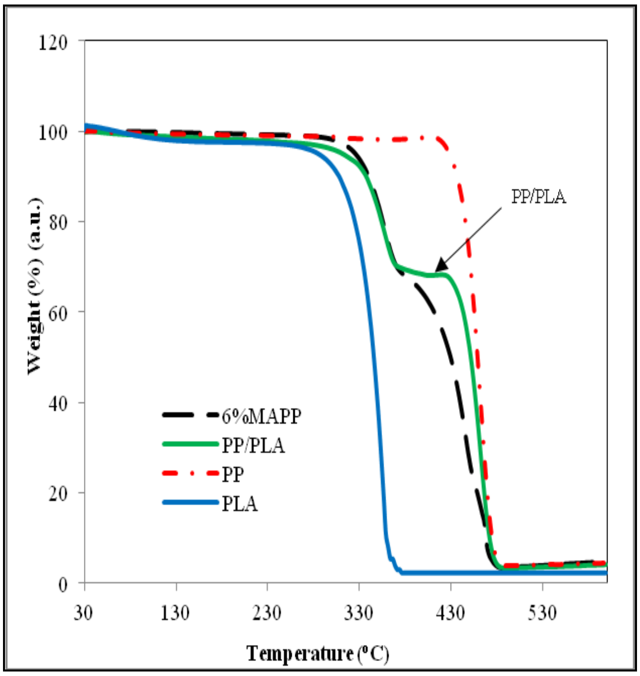

Fig. 3: TGA of PLA, PP, PP/PLA blend and blend with 6 wt% MAPP

Table 3: TGA derived decomposition temperatures

Samples	T_{onset} (°C) PP/PLA	T_{max} (°C) PP/PLA
PP	442	463
PLA	305	357
PP/PLA	336/ 444	368/ 463
PP/PLA/MAPP 6 wt%	338/ 423	367/ 446

3.3. Scanning Electron Microscopy

Tensile fractured surfaces were examined by using Hitachi TM3030Plus scanning electron microscope (SEM) with an acceleration voltage of 15kV; SEM images were shown in Figure 4 (a), (b) and (c). Figure 4 (b) shows the appearance of rough and coarse fibrous structure for the PP/PLA blend. However, as can be seen in Figure. 4(c), incorporation of 6 wt% of MAPP, the blend shows much smoother surface. It indicates that, the compatibility between PP and PLA blend was improved.

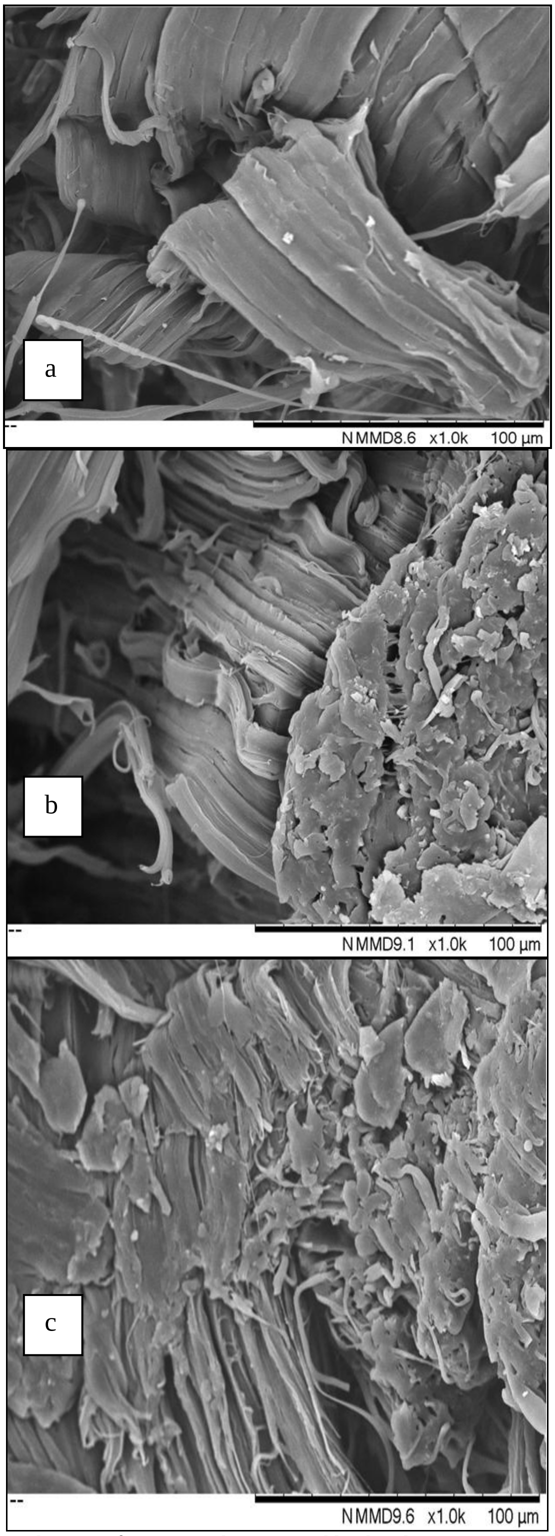

Fig. 4: The SEM for (a) PP, (b) PP/PLA blend and (c) PP/PLA with 6% MAPP

3.4. FT-IR Analysis

The analysis of functions of PP/PLA blends and with a compatibilizer was carried out by FT-IR analysis. The results are shown in Figure 5. For PP/PLA blends of ratios 70/30 the transmittance band that represents PP and PLA were observed in the polymer blends. The transmittance bands of PP shows at 2923cm^{-1} was assigned to C-H stretching.

The transmittance bands of PLA at 1766 cm^{-1} referred to C=O stretching [9]. However, the characteristic spectrum of the ester linkage of MAPP and PLA between 1800 cm^{-1} and 1700 cm^{-1} was not observed.

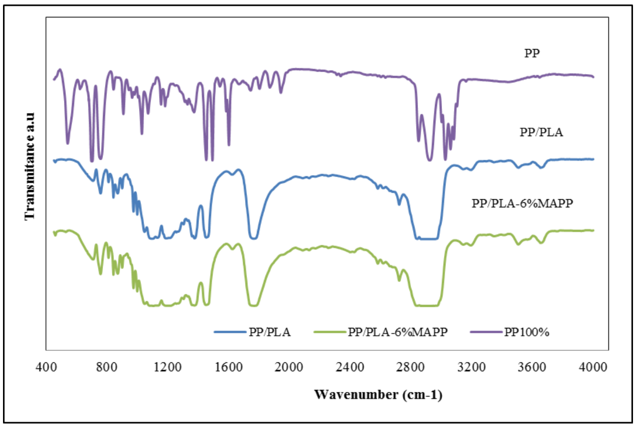

Fig. 5: FT-IR spectra of PP, PP/PLA (70/30) and PP/PLA with 6% MAPP

4. Conclusion

In this study, the effects of compatibilizers on the tensile and impact strengths of the PP/PLA (70/30) blends with the amount of the 3, 6 and 9% MAPP were investigated. From the results it was observed the addition of the 3 to 6% MAPP compatibilizer led to a clear promotion of Young's modulus but slightly increased in tensile strength. However, from the results of impact strength of the PP/PLA (70/30) blends, it is concluded that MAPP doesn't improve the impact strength of the PP/PLA blends. TGA result shows, blending 70 wt.% PP with 30 wt.% PLA cause increased the thermal stability of PLA but no changes in the thermal stability of PP. The presence of 6 wt.% MAPP has decreased the initial weight loss of PP component, T_{onset} from 444 °C to 423 °C. FT-IR analysis shows, the characteristic spectrum of the ester linkage of MAPP and PLA between 1800 cm^{-1} and 1700 cm^{-1} was not observed. SEM image shows, at 6 wt.% of MAPP loading the blend shows much smoother surface. From the above results, it is suggested that the optimum amount of the compatibilizer for PP/PLA (70/30) are in the range of 3 to 6 wt.%.

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