

Effect of Dispersed Phase Particle Dispersion on the Thermal Stability of Recycled Poly(ethylene terephthalate)/Polypropylene Blend

Yew Wei Leong^{1*}, Hiroyuki Inoya², Supaphorn Thumsorn¹ and Hiroyuki Hamada¹

¹*Department of Advanced Fibro Science, Kyoto Institute of Technology, Japan*

²*Yasuda-Sangyo Co. Ltd., Kyoto, Japan*

*Corresponding author e-mail address: leong@kit.ac.jp

ABSTRACT: Blending of recycled polyethylene terephthalate (RPET) from waste bottles with polypropylene (PP) was performed in an attempt to enhance the processability of RPET. The idea of blending RPET with PP sprouted from the intention of recycling PET bottles together with their PP-based caps. Therefore, preliminary blending of RPET with PP (RPET/PP) was performed at various PP and compatibilizer contents. The incorporation of compatibilizers reduced the PP particle size and improved the overall homogeneity of the blends. This effectively reduced stress concentration points and enhanced the mechanical performance of the blends. More importantly, the incorporation of PP into RPET significantly increased the degradation temperature of the blends provided the dispersion of PP phase in RPET was excellent.

KEYWORDS: Recycling, Polymer Blends, Thermal Stability, Compatibilization

INTRODUCTION

Public awareness of environmental and energy problems from plastics wastes has posed a challenge to many research groups to find ways to convert plastic waste into useful materials and product instead of ending up in landfills. Polyethylene terephthalate (PET), which is recognized to be one of the most versatile engineering plastics that are mainly used for producing textiles and soft-drink bottles [1, 2], is also one of the most discarded packaging materials.

In previous works, some efforts were devoted to investigate the possibilities in manufacturing products such as household equipments, structural parts of vehicles, containers, bottles, composite materials, etc. from recycled PET (RPET) through injection, extrusion and thermoforming processes [3]. However, the amount of RPET usage is still very minimal compared to the quantity of discarded PET (mainly from soft drink bottles) because of a difficulty in collecting and separating the PET bottle from the caps and labels prior to recycling. Thus, it is necessary to establish an efficient and cost-effective recovery method that can convert post-consumer PET bottles (including the caps) into useful products in packaging, commodity and engineering filed. To do this, we recognized the importance to blend RPET with PP since most caps are made from the latter material.

PET and PP are incompatible due to differences in chemical structure, whereby the former is known to be a polar polymer while the latter is non-polar. Therefore, their blends would exhibit a two phase morphology whereby the dispersed phase takes the

form of micro-spheres due to weak interfacial interaction. Typically, the strength and stiffness of PET blends is proportional to the PET content, but owing to the phase separation, the blend exhibits very poor impact strength and elongation at break. Previous works have mainly focused on the blending of polyolefins and PET where PET was the minor phase. As such, the processing temperatures were limited to between 200 to 230 °C apparently to avoid thermal degradation [4]. However, very few works have considered producing blends with RPET as the major phase, much less to process these blends at temperatures above 270 °C since it is assumed that polyolefins would undergo thermal degradation. Moreover, considering the average PET bottle to cap weight ratio is 90:10, it is important to develop techniques for producing blends with RPET as the major phase in order to simulate actual recycling scenarios.

In the present work, blending of RPET with various contents of PP and compatibilizer was performed in order to obtain the optimum blend formulation with the best possible mechanical performance. In particular, the effect of compatibilization on the morphological characteristics was elucidated. Since the typical processing temperatures employed for PET and PP are very different, the thermal degradation characteristics of the individual components and the blends were also evaluated in order to confirm the viability of blending RPET and PP at high temperatures.

EXPERIMENTAL

Materials

The RPET was obtained in the form of flakes from crushed post-consumer PET bottles courtesy of Yasuda Sangyo Co. Ltd. Since the caps were separated from the bottles and have all been discarded before the bottles were crushed, the source of polypropylene (PP) from the caps were not available. Therefore, instead of recycled PP, neat PP J900GP (MI = 13, $M_w = 2.3 \times 10^5$) obtained from Idemitsu Petrochemical Co., Ltd., Japan, was incorporated into RPET. Styrene-ethylene-butadiene-styrene-based terpolymer (SEBS) was used as a compatibilizer at loadings of between 1 to 7 phr. Specimen compositions are listed in Table 1. Only RPET/PP blend compositions of 95/5 and 90/10 (after referred to as 95/5 and 90/10 blends) were chosen based on the PET/PP content of a drinking bottle with a cap (for 500 and 1250 ml bottles).

The RPET and PP were dry-blended prior to compounding in a single screw extruder (SRV-P500, Nihon Yuki Co., Ltd.) set at a barrel temperature between 265-290°C and screw rotation speed of 430 rpm. The extrudate was pelletized and molded into dumbbell specimens by using a 50-ton injection molding machine (UM50, PO YUEN Machinery Co. Ltd.). The maximum barrel temperature, mold temperature, and injection speed was set at 285°C, 30°C and 100 mm/s, respectively.

Morphological Observations

Morphological observations were performed on the e cross-sections of cryogenically-fractured pellets by using a scanning electron microscope (SEM), JSM-5200 (JEOL Japan Co. Ltd.). From the high magnification SEM images, the size (area) of the PP particles were measured by using an image analysis software (Image J). From these measurements, the volume average diameter, d_v , for at least 200 dispersed phase particles in each material composition were calculated through the following equation:

$$d_v = \frac{\sum N_i d_i^4}{\sum N_i d_i^3} \quad (1)$$

where N_i is number of particles having a diameter d_i . Tensile fractured surfaces of injection molded samples were also subjected to microscopic examination and the particle size distribution was found to resemble that of the pellets.

Thermogravimetry Analysis (TGA)

The thermal degradation characteristics of the individual components as well as the blends were evaluated by using a TA Instrument TGA2950 high-resolution modulated thermogravimetric analyzer. About 10 mg of RPET, PP, compatibilizer and their blends in pellet form were heated from room temperature to 600 °C by employing a high-resolution temperature ramp feature to accurately pinpoint the onset degradation temperatures. All samples were analyzed in dry air.

RESULTS AND DISCUSSION

PP Particle Size and Distribution in RPET

Effect of Compatibilizer Content

Figure 1 depicts the morphological characteristics of RPET/PP (95/5) blends upon the incorporation of compatibilizers at varying concentrations. Significant changes to the size and distribution of the PP phase could be observed as the content of compatibilizer was increased from 1 to 7 phr. The smaller dispersed phase particle and cavity sizes could have made the crack propagation path more complicated and promoted crazing during tensile and impact loading.

The volume average particle diameter, d_v that was calculated from equation (2) is plotted in Figure 2. In the un-compatibilized blend, a broad distribution of large PP particles can be observed in both the skin and core regions due to the instability and coalescence of the PP phase during melt mixing. However, the number of large particles was far more prominent in the core region as compared to the skin irrespective of PP content in the blend. When only 1 phr of compatibilizer was added to the 95/5 blends, the PP particle size distribution became significantly narrower while the d_v values experienced a significant reduction of about 50% at the skin and 22% at the core. By increasing the compatibilizer content up to 7 phr, the particle size distribution at the skin became much narrower although the d_v values remained similar. This is an indication that the particles at the skin have already attained the smallest possible size with a minimum d_v value of about 0.65 μm . Meanwhile, the particle size at the core regions gradually decreased towards a similar minimum d_v value at the skin with increasing compatibilizer content. Similar compatibilization effects have also been reported elsewhere for other polymer blend systems [5, 6].

Thermal Stability of RPET, PP, Compatibilizer and their Blends

From thermogravimetric analysis (TGA) results, the onset degradation temperature (T_{onset}) of RPET pellets in air was recorded at 340 °C and the broad derivative peaks indicate a gradual degradation of RPET, which is mainly due to hydrolysis. Therefore, RPET is not expected to degrade at the designated processing temperature of 285 °C during injection molding as well as compounding. However, the respective T_{onset} recorded for neat PP and compatibilizers were 257 °C and 275 °C. The sharp derivative peaks following T_{onset} for these components suggest that both materials would degrade

at a very high rate mainly due to oxidative reactions. Hence, these components would be extremely unstable and volatile if they were to be processed individually at 285 °C.

However, when these components were heated in nitrogen atmosphere, the T_{onset} for all components increased significantly. The most notable improvement in thermal degradation resistance was in PP where a 140 °C increment from a T_{onset} of 258 °C could be observed. Even the T_{onset} of the compatibilizer was increased to 326 °C from 275 °C with the absence of oxygen. This is a strong indication that both PP and compatibilizer are extremely sensitive to oxidative degradation but they can nevertheless be processed at high temperatures should their exposure to oxygen be limited.

Interestingly, when TGA was performed on RPET/PP/compatibilizer blends in air, the T_{onset} of PP and compatibilizer were absent, as could be observed in [Figure 3](#). Furthermore, the T_{onset} of the blends recorded at above 355 °C were even higher than that of monotonic RPET. It is also interesting to note in [Figure 4](#) that higher PP content in the blend could also result in an increase in T_{onset} of the blends despite the apparent immiscibility and phase separation between PP and RPET. The apparent increment in T_{onset} of the blends is attributed to the excellent barrier properties of RPET, which limited the exposure of PP and compatibilizer to oxygen and therefore preventing extensive degradation of these phases. The dispersed phases, on the other hand, were able to enhance the overall thermal degradation resistance of the blend provided they are homogeneously dispersed.

The effect of PP particle size (d_v) on the T_{onset} was elucidated and presented in [Figure 5](#). Since the onset of degradation would most likely occur from the surface of the pellets, the d_v values at the skin region of the pellets are presented. From the results, it could be deduced that smaller PP particle size at the skin region was effective in suppressing thermal degradation of the blends. Therefore, it should be noted that good thermal stability of the blends can be achieved provided excellent homogeneity and small PP particle size (preferably in the submicron range) can be obtained in the pellets.

CONCLUSIONS

In this investigation, the PP minor phase particle dispersion was found to be vastly different at the skin and core regions of the pellets as well as injection molded specimens. The PP particle size and homogeneity of the RPET/PP blends could be modified by the use of compatibilizers and this would profoundly influence the mechanical properties as well as thermal stability of the blends. At an optimum compatibilizer content of 5 phr, the PP particle size in the blends would be mostly in the submicron range while excellent overall homogeneity could be achieved. This level of particle dispersion and homogeneity was the key towards obtaining blends with excellent mechanical performance and enhanced thermal resistance. This information will be very useful for the PET waste bottle recycling industry since it provides the possibility of recycling the bottles even without first separating the PP caps and yet able to obtain blends with enhanced properties.

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Table 1: Specimen designation and Izod impact strength of RPET/PP blends at various PP and compatibilizer contents

Sample	Composition		
	RPET (wt%)	PP (wt%)	Compatibilizer (phr)
100/0	100	0	0
95/5	95	5	0
90/10	90	10	0
70/30	70	30	0
0/100	0	100	0
95/5/1	95	5	1
95/5/3	95	5	3
95/5/5	95	5	5
95/5/7	95	5	7
90/10/1	90	10	1
90/10/3	90	10	3
90/10/5	90	10	5
90/10/7	90	10	7

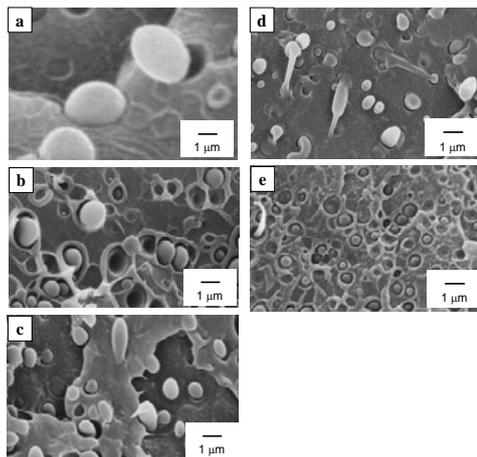


Figure 1: SEM photographs showing PP dispersed phase size in 95/5 blends at various compatibilizer contents: (a) 0 phr; (b) 1 phr; (c) 3 phr; (d) 5 phr; (e) 7 phr

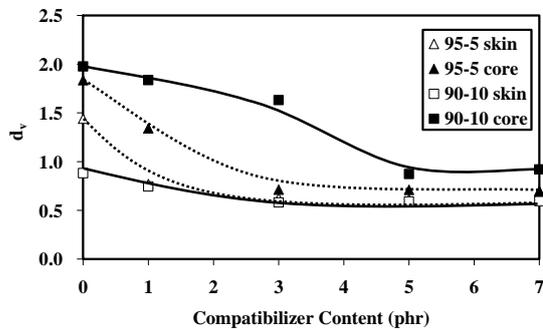


Figure 2: Volume average PP particle diameter (d_v) of 95/5 and 90/10 blends at various compatibilizer contents.

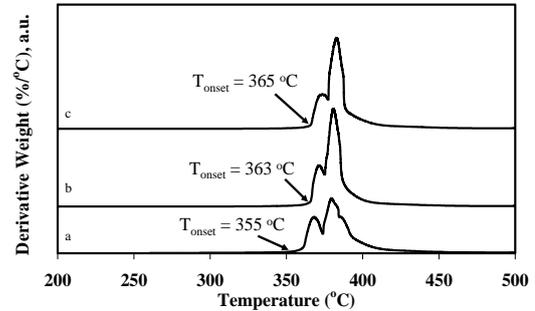


Figure 3: Effect of compatibilizer content in 95/5 blends on the T_{onset} during thermogravimetric analysis in air. Compatibilizer content = (a) 0 phr; (b) 3 phr; (c) 5 phr

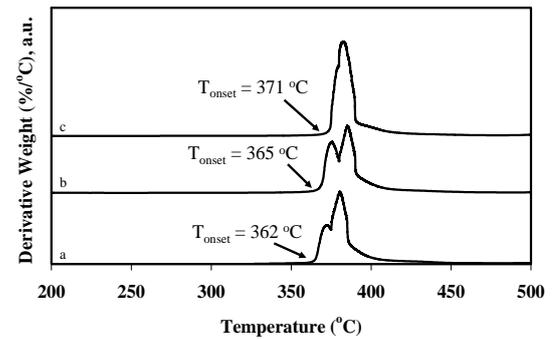


Figure 4: Effect of compatibilizer content in 90/10 blends on the T_{onset} during thermogravimetric analysis in air. Compatibilizer content = (a) 0 phr; (b) 3 phr; (c) 5 phr

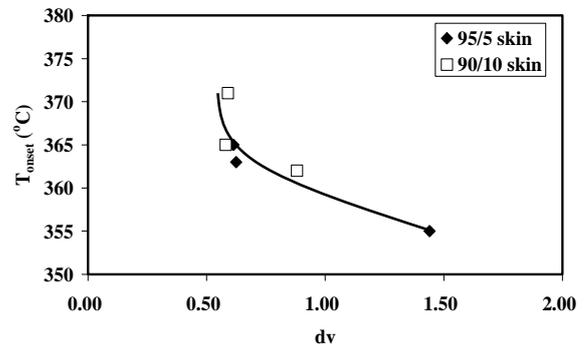


Figure 5: Influence of PP particle size (d_v) on T_{onset} of both 95/5 and 90/10 blend pellets