Effect of Additives on Processing and Physical Properties of Recycled Polyethylene Terephthalate (RPET)

by

Mark Kegel
Dr Igor Sbarski, IRIS
Dr Pio Iovenitti, IRIS
Assoc. Prof. Syed Masood, IRIS
Adjuct. Prof. Edward Kosior, Visy Plastics Pty. Ltd.

Abstract

This paper describes the effect of individual additives that are present in typical masterbatch formulations; the role they play in modifying physical properties and processability of blends based on RPET. Additives such as titanium dioxide, carbon black, linear low-density polyethylene and polyethylene wax are often incorporated into the composition of masterbatch. Blends based on these additives have been analysed for shifts in thermal transition points, levels of crystallinity and physical properties such as tensile and impact strength. The results show that, at the addition rates used, some additives had significant effects on processability and crystallinity, negligible effects on physical properties and antagonistic effects were noted when additives were combined.

1. Introduction

1.1 Overview

In the last decade there has been a growing demand for RPET, primarily from post consumer sources going into the fibre, packaging and other plastic manufacturing industries. In many of these industries, acceptance or changeover has been slow due to the lack of knowledge and experience in dealing with RPET. The first consideration is the drying requirements for RPET, which has received significant coverage in other publications [1,2]. The aim of this paper is to address some of the questions about the effect individual components of the masterbatch formulation have on a RPET system. Can the conventional masterbatches be used with RPET? What will be the effect on the product? To illustrate this, IRIS has conducted experiments with a number of common masterbatch components and observed their effect on the processing, physical and thermal properties of RPET.

1.2 Effect of Additives

Additives play a crucial part in all plastics. Be it to colour the resin, in the form of fillers, a carrier for other additives or as a lubricant. Each additive serves a role that improves certain features that are crucial to processing, physical strength or appearance. Authors such as Cheng and Shanks [3] have looked at the effect of fillers such as carbon black, TiO_2, glass fibre, $CaCO_3$, and Kaolin have on the complex crystallisation kinetics of a PET system. This paper is more generic in nature and the outcomes are designed to be more applicable to the processing and production of products using RPET.

1.3 Determination of Crystallinity

The level of crystallinity in PET is an important parameter dictating the major properties of the products made. A few properties that the level of crystallinity in PET effects are low temperature tack, barrier properties, as well as optical clarity. Although many of the applications for RPET such as fibre spinning, injection stretch blow moulding, and biaxially orientated films, do not rely on the thermal crystallisation mechanism. In these production processes thermal crystallisation is less important than strain induced crystallisation [4]. The strain-induced crystallisation has been investigated thoroughly by Salem [5]. Although the products of strain-induced crystallisation can obtain high levels of crystallinity, the product clarity generally remains unchanged.

In other applications where the strain induced on the polymer and cooling during processing are less excessive, such as injection moulding and extrusion, the thermal crystallisation mechanism is important since it is the dominant mechanism for imparting crystallinity to the product. For these applications if the crystallinity of the product needs to be increased, a nucleating agent is normally incorporated. The additives that are being used in this study are fillers (carbon black, TiO_2) and polymers (LLDPE, Wax). The fillers can act as a nucleating agent as has been shown by Chen [1] and the polymeric additives' general function is as a lubricant and transport medium. A problem that can be envisaged by combining these additives is that they may interfere with each other, and due to increased wetting of one of the polymeric phases, the result may be migration or concentration of the fillers in the polymer additive. The polymeric additives that we used are widely known to exist in a separate phase to that of the RPET. Consequently, the nucleating fillers may have limited opportunities to chemisorb or interact with the fillers if another polymeric additive is present.

2. Research Methodology

2.1 Materials

This study used P1MPNC grade of RPET manufactured by the collaborating company, Visy Plastics. This is a grade of RPET that has very low levels of residual contaminants. The additive materials were all supplied by Allied Colour and Chemicals and can be seen in Table 1.

2.2 Method

This study used the common addition rates of additives that are incorporated into a conventional masterbatch formulation. The addition rates of the respective additives are listed in Table 2.

The materials for this research were pre compounded using a 12 mm Axon Pacific laboratory single screw compounding extruder. The RPET and additives were bag mixed and then dried in a conventional oven at 160 ^{o}C for a period of 2 hours. The blends were then compounded using an extruder temperature profile that ranged from 265^{o}C at the feed throat to 285^{o}C at the die.

The pelletised blends were then injection moulded on a Battenfeld PLUS 350 injection moulder. Once again the materials were pre dried before injection moulding. For this drying sequence a vacuum oven was used at a temperature of 160^{o}C and a vacuum of 100mbar. All the blends were injection moulded using the same conditions of temperature 265-285^{o}C, injection pressure 50% and a cycle time of 25 seconds.

Impact testing was conducted on a Ceast Resil Izod impact tester in accordance with ASTM D 256.

Tensile testing was conducted on a Zwick Z010 tensile tester in accordance with AS 1145.

Thermal testing was conducted on a TA Instruments DSC 2920 Modulated DSC, at heating and cooling rates of 15^{o}C per minute in DSC mode. The qualitative analysis of processability was done through observations of surface finish, throughput, stability and amperage during the extrusion compounding of the RPET with the additives. These parameters, such as throughput in kg/hr, amperage in %, were assessed individually and then combined under the heading "processability" to simplify results.

3. Results and Discussion

3.1 Overview

In order to analyse the effect that the addition of low levels of additives have on our RPET system, we have summarised our experimental results and compared the results obtained from the additive blends with those of the unmodified re-extruded RPET. These results can be seen in Tables 3 to 8.

The standard deviations have been taken from the tensile and impact results. The results have been tabulated against the unmodified re-extruded RPET. They have been numbered in order of the standard deviation or for the purposes of this paper we will call this parameter reproducibility. Zero has been assigned to the lowest reproducability and 5 to the highest, and the results appear in Table 9.

3.2 Comparison of thermal and physical results of blends

From the results obtained for the various blends shown in Tables 3 to 8, it can be seen that even at low levels of addition, the additives have an influence on the physical and thermal properties of the RPET. Some of the results cannot be used to draw conclusions due to differences between them being small and within the limit of error in the apparatus. The results for impact strength, elongation and tensile strength at yield and modulus remain unchanged by the additives. This can be expected as the levels of addition are small and therefore their influence on overall physical properties are limited.

The properties where differentiation between the additives can be made are processability, glass transition temperature and the level of crystallinity.

If we use the re-extruded RPET as the standard for comparison, the addition of TiO_2 (Table 5) results in the highest level of crystallinity. The level of crystallinity for the other filler additive carbon black (Table 6) is lower. An explanation for this could be that TiO_2 has sharp surfaces as opposed to the rounded surfaces of the carbon black. The TiO_2 blend produces results that are far better than those of the unmodified RPET in terms of thermal properties, processing and reproducibility.

The addition of LLDPE (Table 7) also produced some of the best results in the series of materials when compared to the unmodified RPET with no additives. The material has a low level of crystallinity and the additive seems to interfere with the crystallisation process. The other key improvements of this blend are the processability and reproducibility of results. The addition of the polymeric additive seems to act in a similar fashion to a lubricant.

The wax blend in Table 8 also has a number of improved properties over that of the unmodified RPET, although they were related to processing and reproducability. This result indicates that the addition of lubricants can improve processing at the cost of the other properties.

On the whole, carbon black in Table 6, and all the additives in Table 4 produced a result that was less favourable than that of the unmodified RPET.

As most masterbatches contain similar ingredients and are added at similar levels to the additives used in our study, we can conclude that a standard LLDPE based masterbatch can be used in RPET colouring, foaming, and other processes.

3.3 Predictability

The predictability of processing RPET can be improved with the addition of TiO_2, LLDPE and wax. The product is a more predictable outcome in terms of the standard deviation of the physical properties in the finished product than that which is obtained with the RPET unmodified blend. However, the addition of carbon black and all the additives together results in larger standard deviations, and therefore less predictable results. The reasons for this are not initially clear. If we compare the processability of the blends we can see that the blends that performed better than the unmodified RPET, also showed improved processing characteristics due to the addition of the respective additives.

4. Conclusions

The main conclusions drawn from this research are:

- The additions of low levels of specific additives can significantly improve the processing of RPET resin

- Additives such as TiO_2 and LLDPE can improve properties, processing and repeatability of results when compared to an unmodified RPET.

- The combination of all the additives produces an antagonistic effect to the stability of processing.

- A LLDPE masterbatch can be used to colour, foam and lubricate RPET.

5. References

[1] Bayer, “Practical information Brochure: Drying, 1994.

[2] Shinkong, “Shinpet PET chips: Users manual”, May 1993.

[3] S. Cheng, R. Shanks, Journ. Of App. Poly. Sci., Vol. 47, 2149-2160 (1993)

[4] N. &P. Cheremisinoff, “Handbook of applied polymer processing technology”, Marcel Dekker, 1996, pg. 666.

[5] D. R. Salem, , POLYMER, 1992, Vol. 33, No. 15, Pg. 3182-3188.

6. Appendix

TiO_2	Tioxide A-HR organically coated titanium dioxide.
LLDPE	Ladene RX6104 Medium density Polyethylene
Wax	Nimelec CWN-201 non polar low density polyethylene wax
CB	Cabot Vulcan P Carbon Black

Table 1 - Additives used in formulations

Additive	Rate (weight %)
TiO_2	0.5
LLDPE	0.9
Wax	0.2
CB	0.06
All	All additives at respective rates of addition

Table 2 - Levels of addition of respective additives

Processability	Poor
Impact Strength (J/m)	29.8
Tensile Strength at Yield (MPa)	57.4
Elongation at Yield (%)	5.3
Modulus (MPa)	1804
Crystallinity (%)	32.3
T_g (^{o}C)	81.6

Table 3 - The properties of re extruded RPET

Processability	Good
Impact Strength (J/m)	28.8
Tensile Strength at Yield (MPa)	56.2
Elongation at Yield (%)	5.4
Modulus (MPa)	1790
Crystallinity (%)	30.1
T_g (^{o}C)	82.5

Table 4 - The properties of RPET with all additives

Processability	Very Good
Impact Strength (J/m)	29
Tensile Strength at Yield (MPa)	56.7
Elongation at Yield (%)	5.2
Modulus (MPa)	1805
Crystallinity (%)	34.7
T_g (^{o}C)	79.9

Table 5 - The properties of RPET with TiO_2.

Processability	Good
Impact Strength (J/m)	28
Tensile Strength at Yield (MPa)	58
Elongation at Yield (%)	5.2
Modulus (MPa)	1805
Crystallinity (%)	32
T_g (^{o}C)	84.9

Table 6 - The properties of RPET with Carbon Black

Processability	Greatly improved
Impact Strength (J/m)	30.2
Tensile Strength at Yield (MPa)	59.9
Elongation at Yield (%)	5.3
Modulus (MPa)	1802
Crystallinity (%)	30.2
T_g (^{o}C)	82.4

Table 7 - The properties of RPET with LLDPE

Processability	Significantly improved
Impact Strength (J/m)	29.2
Tensile Strength at Yield (MPa)	57
Elongation at Yield (%)	5.2
Modulus (MPa)	1771
Crystallinity (%)	33.3
T_g (^{o}C)	80.9

Table 8 - The properties of RPET with Wax

RPET re extruded	2
TiO_2	5
CB	2
LLDPE	4
WAX	3
All additives	1

Table 9 - The relative reproducibility of results