Recycling of Lead Acid Battery Cases Polypropylene in Combination with Thermal Stabilizers and Virgin Polypropylene

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Abstract

In this study, blends of virgin polypropylene (PP) and recycled PP used in lead-acid battery cases at various weight ratios were prepared by a single screw extruder. Melt flow index (MFI) and carbonyl index were measured for evaluation of the changes in chemical structure of the blends during the extrusion process. Oxidative induction time (OIT), was also tested to determine the thermal resistance of the samples. Mechanical properties of the samples were studied by tensile and charpy impact tests. To stabilize the compounds during the extrusion process, combinations of a phenolic (Primary Antioxidant, P-AO) and phosphite (Secondary Antioxidant, S-AO) thermal stabilizers with a metal deactivator (Calcium Stearate, CaSt) were used. An optimum composition of stabilizers in the 40:60 (virgin: recycled) PP blend was obtained by using the Taguchi method design of experiments (DOE). This optimum combination of stabilizers was 1 wt% P-AO, 0.2 wt% S-AO, and 0.5 wt% CaSt. In addition, DOE results showed that the primary antioxidant has the biggest influence on stabilization of PP during the extrusion process. Measurement of OIT parameter of the samples containing optimum combination of stabilizers proved that the thermal resistance of these samples was better than the virgin PP. Carbonyl index measurements of these blends indicated that a little degradation occurred in the extrusion process. The results of impact tests showed that the stabilized 40:60 (virgin: recycled) PP blend containing the optimum combination of stabilizers has the same impact strength as the virgin PP. The tensile test results showed that the stabilization of PP blends with the optimum combination of antioxidants led to the higher elongation at breaks and yield strength as compared to the sample without stabilizers.

Keywords: Recycled polypropylene, Thermal stabilizer, Antioxidant, Metal deactivator, Design of experiments

Introduction

Polypropylene (PP) is one of the most common plastics used in the manufacturing of lead-acid battery cases, where the recycling of the material has become a common practice, being both economically viable and environmentally friendly. During the recycling process, the various components of the spent battery are separated, where the crushed battery case is washed in order to remove any excess acid and lead-containing particles. The plastic components are subsequently melted and extruded into pellets. The use of recycled PP has cost saving implications, but does have a disadvantage in that the material starts to deteriorate during recycling process. The degradation processes of the PP induce decrease of molecular weight, a narrowing of the molecular weight distribution of the polymer and increase of the melt flow index (MFI). Also, in the presence of oxygen, they induce the formation of oxygenated groups like carbonyl and the presence of mechanical stresses accelerates the degradation processes. This means that the mechanical properties of the recycled PP can be lowered after one or more recycling steps [1-8]. Therefore, re-stabilization during the recycling processes is the best method to stop or slow the degradation and then the deterioration of the mechanical properties [9]. Previous papers have shown that the recycling of PP has a detrimental effect on the material's mechanical properties, such as tensile strength and impact, and also on its flow properties during the recycling process [8, 10-15]. However, not much attention has been conferred on the effect of thermal stabilizers with metal deactivators in recycling of the PP used in lead acid battery cases. This study was carried out to evaluate the use of metal deactivators with combinations of thermal stabilizers in recycled PP.

Experimental

Materials

The virgin PP copolymer used in this study was EPC40R with a density of 0.9 g/cm3 and a MFI of 7.5 g/10min, supplied by Arak Petrochemical Co. Recycled PP was obtained from the crushed battery cases after washing with soap and alcohol. The two stabilizers, Anox 20 (Tetrakis-[methylene (3,5-di-t-butyl-4 hydroxyhydro-cinnamate)]-methane) and Alkanox 240 (Tris (2,4-di-t-butylphenyl)-phosphite), were supplied by Gulf Stabilizers Industries Co. Three metal deactivators, zinc and calcium stearate (supplied by Kimiaforooz Co) and Anox MD 1024 (1, 2-bis (3, 5-di-tert-butyl-4hydroxy hydrocinnamoyl) hydrazine), were supplied by Gulf Stabilizers Industries Co.

Blend of virgin PP and recycled PP with different weight ratios (20, 40, 60, 80, 100 wt%) combined with stabilizers, was then melt mixed by a single screw extruder, Brabender, with a temperature profile of 160-180-190-210°C and a screw speed of 100 rpm.

Characterization

- *Melt Flow Index (MFI)*

The melt flow index of all samples was measured with a melt indexer at 230°C under a load of 2.16 Kg according to ASTM D-1238.

- *carbonyl index (CI)*

The carbonyl index was calculated as the ratio of the intensity of the 1740 cm-1 carbonyl peak in the FTIR spectrum to a reference peak such as 1415 cm-1 methyl group. The thin films of PP samples with 15 µm thickness were prepared by hot press (200°C and 100 bar) and analyzed by Bomem FT-IR spectrometers spectralab scientific.

- *Mechanical properties*

The mechanical properties of the samples were measured by tensile and impact test. The tensile specimens were compression molded (at 200°C and 100 bars) and analyzed using a Testometric tensometer, 5 kN load cell at crosshead speed of 50 mm/min according to ISO 527. The notched impact test was run using a Zwick/Roell impact tester with a 2.75 J pendulum according to ISO 180/1A. The tests were performed ten times and the average value was reported in kilojoule per square meter (kJ/m2).

- *Oxidative induction time (OIT)*

Oxidative induction time (OIT) measures the amount of time that a polymer needs to oxidize at an elevated temperature. This parameter was measured using a Netzsch differential scanning calorimeter (DSC), model DSC200F3, at a heating rate of 20°C/min. OIT was measured in oxygen atmosphere with a gas flow of 50 ml/min at a temperature of 200°C.

Design of experiment (DOE)

In the present study, three parameters, namely phenolic (Primary Antioxidant, P-AO), phosphite (Secondary Antioxidant, S-AO) thermal stabilizer and calcium stearate, were selected. Based on Taguchi's orthogonal array, the most suitable array for the current investigation is L9: hence, nine experiments were conducted. Then the MFI testing was carried out to investigate the influence of this Taguchi design of experiment on degradation polymer during the recycling process. In order to determine the optimal level of parameters, analysis was carried out by adopting S/N ratio based on the smaller the better quality characteristic. Finally, a confirmation experiment was conducted to verify the estimation of performance at the optimal parameters obtained from the parameter design.

Results and discussion

Flow characterization

Fig 1 shows the MFI values for ratios of recycled PP with virgin PP for both non-stabilized and stabilized blends. The results showed that the MFI values obtained for the non-stabilized blends were higher than the stabilized blends. The increase in MFI is a direct indication of reduction in molecular weight due to chain scission. Also, in the non-stabilized blends, a drastic increase in the MFI values was observed. It seems that in the non-stabilized blends, adding the virgin PP to the recycled PP not only did not decrease polymer degradation during the extrusion process, but also adding a small amount of recycled PP to the virgin PP caused polymer to degrade rapidly because of the co-presence of the recycled material, which has a high concentration of radicals, hydroperoxide groups; moreover, the presence of metal impurities in the recycled PP accelerates the decomposition of hydroperoxides to free radicals that caused polymer to degrade rapidly. On the other hand, the results showed that this dramatic increase of MFI is drastically reduced by adding the stabilizing agents.

Effect of various metal deactivators

The role of metals and metal-deactivators in polymer degradation is well known [16]. The results showed that, the OIT values obtained for the calcium stearate or commercial metal deactivator was higher than the zinc stearate in combination with thermal stabilizers. It seems that the zinc stearate reduces the effect of the thermal stabilizers, probably because of the unstable complex formed between ligand and metal ions. Table 1 shows the MFI values obtained for the effect of various metal deactivators with thermal stabilizers on blend of virgin and recycled PP. The results showed that the MFI values obtained for the calcium stearate was less than the zinc stearate and commercial metal deactivator, in combination with thermal stabilizers. These results reveal that in any processing, new radicals are generated because of thermomechanical shear among the polymer chains and the mechanical component. This generation of new radicals may be reduced by use of slipping agents such as calcium stearate and zinc stearate, which do not allow the critical stresses to build up, while the commercial metal deactivator does not have such a property. On the other hand, it seems that the zinc stearate reduces the effect of the thermal stabilizers confirming the result obtained by the measurements of the OIT. Calcium stearate seems to show a better efficiency in combination with thermal stabilizers. Also, the results showed that the MFI values obtained for the calcium stearate with commercial metal deactivator and zinc stearate in combination with thermal stabilizers were higher than the non-stabilized recycled PP. This result showed that the calcium stearate alone has the best efficiency in combination with thermal stabilizers.

Carbonyl Index results

The extent of the oxidation of PP during the extrusion process can be evaluated by determining the relative amounts of carbonyl groups present in the material [3,7]. Fig 2, shows the FTIR spectra for non-stabilized and stabilized PP blends. The results show that the carbonyl index values obtained for the non-stabilized blends were higher than the stabilized blends. This implies that the addition of the stabilizers to PP seems to prevent the formation of the carbonyl group during the recycling process. Also, the results showed that in the non-stabilized blend, adding the virgin PP to the recycled PP did not decrease polymer degradation during the extrusion process. These results confirm the results obtained by the measurements of the MFI for describing the rate of degradation of non-stabilized and stabilized PP blends in the recycling process.

Design of experiment (DOE)

DOE results showed that the primary antioxidant (P-AO), secondary Antioxidant (S-AO) and calcium stearate (CaSt), respectively, have the highest effect on reducing the degradation of PP during the extrusion process. Also, by design of experiments, the optimum combination of stabilizer was obtained as: 1 wt% P-AO, 0.2 wt% S-AO, and 0.5 wt% CaSt. On the other hand, the MFI values of 8.1g/10min were obtained by confirming test for the stabilized 40:60 (virgin: recycled) PP blend with the optimum combination of stabilizers.

Mechanical properties

The impact strength and tensile strength results showed that the stabilized 40:60 (virgin: recycled) PP blend with the optimum combination of stabilizers have a similar value to virgin PP. in addition the impact strength and tensile strength of this sample in the absence of stabilizer is near to the recycled PP. This is due to the increase in short chains because of chain scission which are the concentrates of impact energy causing fracture.

Conclusion

MFI can be a useful method to describe the degradation of polypropylene during the extrusion process. The results showed that adding a small amount of recycled PP to the virgin PP caused polymer to degrade rapidly. The results of mechanical tests showed that the stabilized 40:60 (virgin: recycled) PP blend with the optimum combination of stabilizers had mechanical properties similar to virgin PP, while the mechanical properties of this sample in the absence of stabilizer were near the recycled PP.

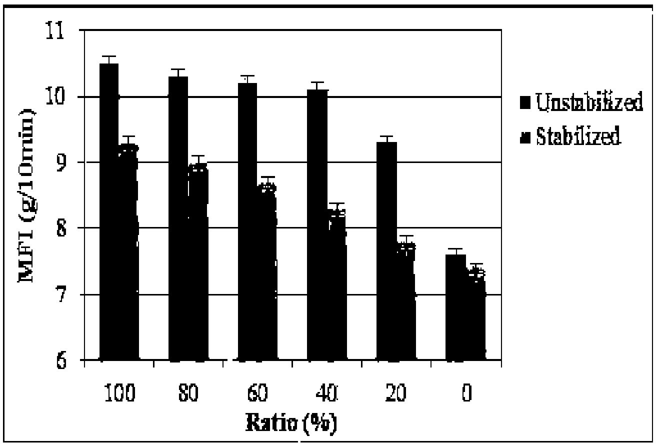

Fig 1: MFI values obtained for ratios of recycled PP with virgin polypropylene.

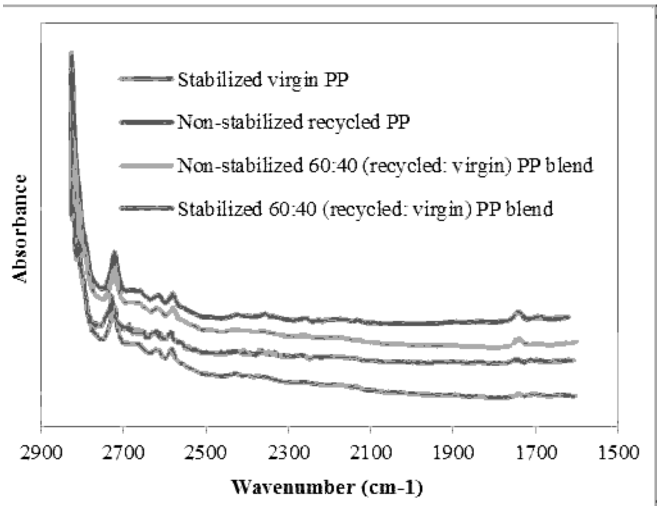

Fig 2: FTIR spectra of non-stabilized and stabilized PP blends.

Table 1: MFI values obtained for various metal deactivators with thermal stabilizers on the 80:20 (recycled: virgin) PP blend.

Recycled PP	Virgin PP	Primary Antioxidant	Secondary Antioxidant	Calcium stearate	Zinc stearate	Commercial metal deactivator	MFI (g/10min)
80	20	-	-	-	-	-	10.3
80	20	0.5	0.5	1	-	-	9
80	20	0.5	0.5	-	1	-	9.7
80	20	0.5	0.5	-	-	1	10
80	20	0.5	0.5	1	-	1	11.7
80	20	0.5	0.5	1	1	-	11.2

References

[1] H. Hinsken, S. Moss, J. R. Pauquet, H. Zweife, *Polymer Degradation Stability*, **1991**, *34*, 279-293.
[2] G. G. Echevarria, J. I. Eguiazabal, J. Nazabal, *Polymer Degradation Stability*, **1996***, 53.* 1-8.
[3] V. A. Gonzalez, G. N. Velazquez, J. L. A. Sanchez, *Polymer Degradation and Stability*, **1998**, *60*, 33–42.
[4] A. R. Filho, S. H. P. Bettini , A. S. Babetto, L. C. D. Mello, *polymer recycling* , **1998**, *Vol. 3* , No. 2.
[5] I. Loeradana, P. scarafato, D. acierno, *Polymer engineering and science*, **1999**, *vol. 39*, No. 4.
[6] J. Aurrekoetxea, M. A. Sarrionandia, I. Urrutibeascoa, M. L. Maspoch, *Polymer*, **2001,** *44*, 6959-6964.
[7] Q. Xiang, M. Xanthos, S. H. Mitra, J. Patel, *Polymer Degradation and Stability*, **2002**, *77*, 93–102.
[8] N. Rust, E. E. Ferg, I. Masalova, *Polymer Testing*, **2006**, *25*. 130-139.
[9] M. Marrone, F. P. L. Mantia, *Polymer Recycling*, **1996**, *Vol. 2*, No. 1.
[10] Q. Xiang, M. Xanthos, *Polymer Degradation and Stability*, **2002**, *77*, 93–102.
[11] A. Jansson, K. Moller, T. Gevert, *Polymer Degradation and Stability,* **2003**, *82*, 37–46.
[12] K. Ashwini, A. Sanjeev, K.Singh, A. Utreja, *Journal of applied polymer science*, **2004**, *92*, 3247-3251.
[13] M. Hamskog, M. Klugel, D. Forsstrom, *Polymer Degradation and Stability*, **2006**, *91*, 429–436.
[14] M. Helson, V. D. Costa, M. Ramos, G. D. Oliveira, *Polymer Testing*, **2007**, *26*, 676-684.
[15] P. Brachet, L. T. Hoydal, E. L. Hinrichsen, F. Melum, *Waste Management,* **2008**, *28*, 2456-2464.
[16] Z. Osawa, *Polymer degradation and stability*, **1988**, *20* . 203-236.