Available online at www.sciencedirect.com
ScienceDirect
Polymer Testing 26 (2007) 1001–1014
POLYMER TESTING
www.elsevier.com/locate/polytest

Material Behaviour

The effect of Pb and other elements found in recycled polypropylene on the manufacturing of lead-acid battery cases

E.E. Ferg*, N. Rust

Department of Chemistry, Nelson Mandela Metropolitan University, P.O. Box 77000, Port Elizabeth 6031, South Africa

Received 24 May 2007; accepted 2 July 2007

Abstract

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 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 that are then blended with virgin material to injection mold new battery cases and lids. This study showed that a significant amount of lead-containing particles in the form of lead dioxide and lead sulfate remain in the recycled plastic, and are evenly distributed throughout the polymer matrix. TEM studies showed that the particles are less than 1 μm in size and X-ray diffraction analysis of ashed recycled PP samples showed the presence, amongst others, of talc, calcium carbonate, rutile and iron oxide. These compounds come from a range of fillers, flame-retardants, colorants and impurities that originated from the various original battery cases that were recycled. The study showed that modern X-ray fluorescence (XRF) analysis is a quick and reliable method to quantify the amount of the elements found in the plastic and that the concentration of Pb in the plastic can be used as a type of "tracer" to determine the amount of recycled PP used in the manufacturing of a particular battery case. The study also showed that there is possible environmental contamination, in particular with Pb and Br contained in recycled PP during the injection molding process and the burning of the plastic. The Pb- and Br-containing particles are small enough to become air-borne during the burning process of the plastic, resulting in them being part of the soot and other hydrocarbon oils that are emitted. No Pb was observed in the gases emitted during simulated low-temperature injection molding conditions; however, a significant amount of Br was detected in the gases at the lower temperatures. Clear environmental waste classification of the battery case plastic should be done before its final incineration where the amount of trace metals present and its possible contamination to the environment should be considered. Care should also be taken for machine operators who work with the recycled plastic, that no excessive exposure to the halogenated compounds is experienced.

Keywords: Recycled polypropylene; Lead-acid battery; XRF

1. Introduction

Polypropylene (PP) has become one of the most common plastics used in the manufacturing of automotive and some industrial lead-acid battery

*Corresponding author. Tel.: +27 41 504 3160; fax: +27 86 519 3597.
E-mail address: ernst.ferg@nmmu.ac.za (E.E. Ferg).

0142-9418/$ - see front matter
doi:10.1016/j.polymertesting.2007.07.001

casings. Before the commercialization of PP as battery case material, the outer casings of lead-acid batteries were made from synthetic rubber, while some of the casings of large industrial batteries were even made from silica glass. Since the early 1970s, PP has been used for almost all shapes and sizes of lead-acid battery casings and lids, especially for the automotive portable batteries [1]. In general, the properties of PP are well suited for their use as battery case material, where it can withstand the harsh environmental conditions under particular applications. These include a wide temperature range (−32 to 80 °C); chemical resistance to acid, fuel, oils and antifreeze; physical shock; good elasticity and low mold shrinkage to accommodate other material components such as lead post terminals.

Due to the short life-span of a typical automotive battery (2–4 years) and with the increase of its end-user consumption, stricter environmental legislation was introduced concerning its use, disposal and the recycling of heavy metals such as lead (Pb). This has resulted in the complete recycling of the battery in terms of its content where the Pb alloy, oxide and sulfate materials are regenerated for their reuse in electrode manufacturing. The electrolyte or acid is neutralized and the battery case housing is recycled and reused for the manufacturing of battery cases. The recycling of the complete battery has become very efficient where up to 90% of the batteries manufactured are returned and the recycling loop is well managed in most countries that have lead-acid battery manufacturers [2,3].

The recycling process of the lead-acid battery starts at the point where the old battery is returned to the distributor. The batteries are crushed using toothed stainless-steel rollers where the Pb, PP casings and polyethylene separators are separated by floatation due to their respective differences in densities. The heaver lead fraction is removed and reduced back into lead ingots, whereafter it is refined and redistributed back to the Pb-acid battery manufacturers. When the crushed PP is separated from the other components of the lead-acid battery, the chips are extensively washed in order to eliminate any traces of lead-containing particles and acid which might have collected on its surface. The washed chips are then fed into an extruder where they are melted at approximately 245 °C. The molten polymer is then pushed through a die (190 °C) after which it solidifies and the extruded plastic is then pelletized. The high melting temperature of the extruder allows for complete mixing of all chips that originate from a variety of battery case types and speed up the recycling process. The flow diagram in Fig. 1 summarizes the recycling process of the lead-acid batteries.

Previous studies have shown that the reusability of the polymer is limited in terms of how often PP can be recycled [4]. It was shown that a simple lab technique such as a melt flow indexer (MFI) can be used to monitor the amount of recycled material present in a battery case if the MFI of the original virgin and recycled PP is known. The results were in agreement with other published studies in that the recycling of PP has a detrimental effect on the material's physical properties, such as impact and tensile strength, and also on its flow properties during injection molding [5–7]. A common practice in manufacturing is to blend recycled with virgin PP in order to maintain the integrity and physical properties of the final component. This reduces the detrimental effect of using recycled material and allows the use of relatively similar materials when sealing the cover to the battery case.

The waste recycling process is also regulated by the Environmental Protection Agency in terms of the volatile emissions generated during processing and the final disposal of the material, in particular VOCs and halogens [6]. If and when the spent recycled PP is considered as non-recyclable, it would either be disposed of as land-fill waste or incinerated. EU regulations have introduced the restrictions of hazardous substances directives (RoHS) and the waste electrical and electronic equipment directive (WEEE) that apply limitations of certain heavy metals present in plastic components and paints used by consumers. Guidelines are given for the recycling of the complete Pb-acid battery, but there are no clear directives for the requirements and environmental monitoring of various heavy metals found in the plastic components themselves that have become "non-recyclable".

With the recent development of small-scale instrumentation, and the advancement of computer processing power, manufacturers of analytical equipment such as X-ray fluorescence (XRF) have developed portable small-scale instrumentation that allows for the analysis of samples in a quick and non-destructive manner. The instruments make use of small-scale X-ray tubes or radioactive isotopes to excite trace elements in a bulk matrix for their quantitative determination at concentrations levels as low as 10 ppm. The element is identified by its