Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Improved properties of recycled polypropylene by introducing the long chain branched structure through reactive extrusion

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ARTICLE INFO

Article history:
Received 19 December 2017
Revised 1 March 2018
Accepted 25 March 2018
Available online xxxx

Keywords:
Recycled polypropylene
Branched chain
Reactive extrusion

ABSTRACT

An approach originated from preparing long chain branched polypropylene (PP) was applied to modify the properties of recycled PP that involved reactive extrusion to introduce a branched chain structure onto recycled PP under the assistance of chemical reaction between maleic anhydride (MAH) monomer and glycidyl methacrylate (GMA) grafts. The results from Fourier transformed infrared spectroscopy (FTIR) indicated the reaction took place during melt mixing, and the intensity of ester increased with increasing amount of MAH. Several rheological plots including complex viscosity, storage modulus, loss modulus, loss tangent and Cole-Cole plot were used to investigate the rheological properties of recycled PP and modified PP with MAH, which indicated an additional longer relaxation time that was not shown in recycled PP. The effects of branched structure on melting and crystallization behaviors were also investigated, demonstrating the branched chains acted as nucleating agent. Moreover, the branched structure of modified samples gave rise to enhance mechanical properties, especially, the higher impact strength compared with recycled PP.

1. Introduction

Polypropylene (PP), an important polymer in modern society, has been widely prepared and used in our daily life owing to its low density, good processability, better mechanical properties and chemical resistant (Dong et al., 2013; Treadwell et al., 2006). Various PP fabrications processed by injection molding, film extrusion, compression etc. have been produced to meet people's daily needs, such as automobile industry, electronic devices and household appliances etc. (Dányádi et al., 2007; Duquesne et al., 2008; Liu and Qiu, 2013; Luyt et al., 2009; Martín et al., 2011; Ono et al., 2005). Unfortunately, these products interacted with oxygen, photo as well as heat indeed undergo degradation to a different extent during use, which results in the decrease of comprehensive properties, especially the lower mechanical properties compared with virgin composites (Ismail et al., 2008; Rajakumar et al., 2009; Yakimets et al., 2004) and lots of waste solid materials.

At present, the recycling of waste plastics, an efficient way to manage and treat waste plastics, has become a significant section of industry as plastics are now involved in every aspect of our living. There are four main techniques for recycling of waste plastics including primary recycling, mechanical recycling, chemical recycling and energy recycling (Al-Salem et al., 2009, 2010; Ha and Kim, 2012). Certainly, it is very clearly useful for our society to recycle PP products and other polymeric products as much as we can to offset the environmental pressure and relieve the consumption rate of nature resource. Plastic recycling is an economic and valuable practice to save the cost of 20–50% from the point of market price in comparison with their virgin materials (Gu et al., 2017). However, during recycling waste plastic, lots of recycled polymeric products including PP are still disposed of in a landfill or incinerated (Ardanuy et al., 2012; Gregorová et al., 2005), leading to the secondary pollution or shortage of landfill space finally. Faced with the pressure of environmental problems and recycling of waste PP materials, many scientific investigations have been carried out including the simulation of PP aging in the laboratories (Morlat et al., 2004; Zhao and Li, 2006), the stability of recycled PP under experimental conditions (Nasir et al., 2011) and the modification of recycled PP with additives (AlMaadeed et al., 2012; Ares et al., 2010; Chun et al., 2013; Elloumi et al., 2010), which aims to illustrate the mechanism of degradation and provide guidance for industrial utilization in recycled PP.

Based on the modification in recycled PP, there is no doubt that the high quality of recycled PP is achieved after incorporating additives, showing similar or improved performance in comparison with neat PP. For instance, Tri Phuong et al. (2008) investigated the effect of different nano-clay concentrations on the mechanical

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https://doi.org/10.1016/j.wasman.2018.03.040
0956-053X/

properties of recycled-PP/nano-clay nanocomposite. The results showed in their work that the impact and tensile strength could be reached the optimal values and even were higher than those of virgin PP when the contents of nano-clay and compatibilizer (PP grafted with maleic anhydride) were 4 wt% and 20 wt%, respectively. Khanjanzadeh et al. (2011) investigated the effects of organoclay platelet contents (0, 3 and 5 wt%) and PP type (virgin and recycled PP) on the mechanical properties of PP/wood flour composites. The results indicated that the tensile strength and flexural properties of the composites were optimal when the content of organoclay was up to 3 wt%. Especially, it was also found the mechanical properties of recycled PP-based composites were comparable statistically with those of virgin PP. The mechanical properties of recycled PP can be improved through many approaches like adding chemical modified inorganic fillers, incorporating elastomers or blending with other polymers (AlMaadeed et al., 2014; Brachet et al., 2008; Jose et al., 2010; Mural et al., 2011). However, to achieve the desired mechanical properties, the compatibility between recycled PP matrix and these additives should be taken into consideration in the process of modifying recycled PP. These additives must be finely and homogeneously dispersed in polymer matrix as the result of introducing compatibilizer to system. Their addition for modification of recycled PP may result in an increase in the cost of the materials to an extent. Aside from the better results of recycled PP using these additives, there is a tough challenge about the composition of materials during the recycling of PP wastes, leading to phase separation and poor mechanical properties because of the immiscibility for most plastics (Kamleitner et al., 2017). On the other hand, given the fact that recycled PP undergoes the β-scission due to the effects of oxygen, heat and light during degradation and exhibits lower comprehensive properties, filling (or blending) modification of recycled PP with an amount of additives often neglects the major factor (that is to say the β-scission) which induces drawbacks to PP matrix.

To remedy these drawbacks for improving comprehensive performance of recycled PP, we benefited from the ways originated from preparing the long chain branched PP (LCB-PP) in many researches and decided to introduce the branched structure onto recycled PP by reactive extrusion. The reactive extrusion process is favorable due to its advantages such as fast reaction, continuous process (Moad, 1999). The extrusion process is supposed to be a better way to treat waste plastics because of its low cost and accessibility to industrialization, which has gained considerable interest compared with other recycling in terms of energy use and a number of environmental concerns during the energy recovery. Moreover, the formation of long chain branched structure is generally viewed as an approach to improve melt and rheological properties owing to higher molecular weight and more entanglements between molecular chains (Li et al., 2012; Zhang et al., 2012). Apart from meditating rheological and melt properties, the presence of long chain branched structure may provide an opportunity to modify mechanical properties of PP (Li et al., 2012). Cao et al. (2016) prepared LCB-PP vas reactive extrusion and reported that the LCB-PP significantly improved impact strength and yield strength compared with virgin PP. Therefore, to our best knowledge, it seems that the scission chains of recycled PP may be "reconnected" under the assistance of branched points by the formation of chain branched structure, which could offer the possibility to modify comprehensive properties of recycled PP and extend its applications like blow molded films and foams in recycling process.

Glycidyl methacrylate (GMA) contains bifunctional character: a free radically reactive double bond together with an epoxy group that is highly electrophilic and capable of reacting with a number of other functional groups such as carboxyl, hydroxyl, anhydride and amine (Cartier and Hu, 1998; Chen et al., 1996). Therefore, the modification of recycled PP could be carried out under the assistance of reaction between GMA grafts and maleic anhydride (MAH), which could improve the matrix properties and achieve better compatibilization with other additives such as fillers, recycled polyamide and recycled poly (ethylene terephthalate) etc. to a certain extent. In the present study, the recycled PP with branched structure was prepared in the presence of recycled PP grafted with GMA (rPP-g-GMA) and a functional monomer, MAH by the melt extrusion. The melting and crystallization behaviors of samples was investigated, and the linear viscoelastic properties for these samples were further characterized. Moreover, the improved mechanical properties of samples, especially impact strength, was demonstrated by the formation of branched structure in modified samples.

2. Experimental

2.1. Materials

Different samples studied in this work were prepared with recycled PP from waste household appliances. The recycled PP, containing 21.3 wt% of inorganic filler, was kindly supplied by Xin Huanbao Co., Ltd (Guangdong, China). Its main properties are listed in Table 1. GMA was obtained from DOW Chemical Co., Ltd. MAH was acquired from Fuchen Chemical Co., Ltd (Tianjin, China). Antioxidant was the type of Irganox 1010 (Ciba). Other reagents including 2-methylimidazole (2-MI), styrene (St) and dicumyl peroxide (DCP) were used without further purification.

2.2. Grafting procedure

Recycled PP grafted with GMA (rPP-g-GMA) was prepared by melt extrusion in our laboratory with a ϕ36 mm twin-screw extruder (SHJ-36, Nanjing Cheng Meng Machinery Co. Nanjing, China) at 72 rpm. Before extrusion, the recycled PP was dried at 90 °C for 8 h. The formulation of rPP-g-GMA is as follow: 2 kg of recycled PP is mixed with 80 g of GMA, 80 g of St and 4 g of DCP. The peroxide DCP was added to the liquid monomers (GMA and St). The resulting mixture was premixed with recycled PP in a beaker for about 30 min. The final mixture was charged into the extruder at the temperature range of 180 ~ 190 °C. The processed grafts were cooled in cold water, granulated and dried in vacuum under 80 °C for 24 h. Additionally, the grafting degree of rPP-g-GMA was 0.85% after purification and chemical titration.

2.3. Sample preparation

For even dispersion of MAH, 2-MI and antioxidant, these were dissolved in acetone, and this solution was added to self-made grafts. After evaporating acetone, the modified samples with MAH monomer were extruded at 170–200 °C of barrel temperature profile. The detailed composition of modified samples is listed in Table 2. The polymer stripe left the extruder was cooled in water and cut into pellets. These pellets were injection-molded into standard samples for further characterization using an injection molding machine with a temperature range of 190–210 °C. Prior to injection-molding, the material was dried in an oven at 80 °C for 12 h.

Table 1
Physical properties of recycled polypropylene.

Properties	Values
Tensile strength (MPa, GB/T 1040–2006)	21.85
Melt flow rate (g/10 min, 235 °C, 2.16 kg)	12.24
Izod impact strength (nothed, kJ/m^2, GB/T 1843–2008)	1.62
Melting point (°C)	161.87
Density (g/cm^3)	0.92

Please cite this article in press as: Li, Y., et al. Improved properties of recycled polypropylene by introducing the long chain branched structure through reactive extrusion. Waste Management (2018), https://doi.org/10.1016/j.wasman.2018.03.040