Effective Identification on Adulteration of Polyethylene With Post-consumer Ones

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Abstract. This paper mainly describes the effective identification of the adulteration of polyethylene with post-consumer ones. Degradation would be happened when multiple processings occurred. The melt flow index (MFI) analysis, thermal gravimetric analysis (TGA), differential scanning calorimeter (DSC) were used to characterize the processability and thermal stabilities of virgin polyethylene and recycled polyethylene which adulterated post-consumer PE. The results indicated that MFI of PE increased with the increasing doping content. Adulterating reclaimed PE had effects on the thermal stability of PE, which led in lower thermal decomposition temperature. Melting peak of recycled LLDPE varied from merely single to double, which differently compared with virgin LLDPE. Besides, with the doping content of post-consumer LDPE, the melting temperature had a decreasing tendency.

1. Introduction

Plastics are widely used in food and drug packaging industry due to their intrinsic good properties such as light weight, excellent chemical stability, convenient processing etc.[1–3] Food outer packaging, food inner packaging films, beverage bottles, drug bottles and infusion bags are commonly used plastic materials. Virgin plastic granules should be chosen to be used to manufacture food and drug packaging in order to ensure the food and drug safety. Recycled plastics are strictly forbidden to product the food and drug packaging. Because the ingredient of reclaimed PE was sophisticated, and the properties of those reclaimed ones had a reduction.[4–6]. For this reason, research on the effects on the structure and properties of food-grade reclaimed plastics has significance[7–8]. In this thesis, multiple reprocessings were performed by using twin-screw extruder. A series of recycled PE samples
which adulterated a few post-consumer PE were prepared by high-speed commixture and melt extrusion. The aim of this work was to identify the adulteration of polyethylene with post-consumer ones.

2. Experimental

2.1 Materials. Virgin PE and recycled ones were prepared in this study. The recycled PE were carefully washed and dried. The materials are presented in Table 1.

| Type       | Commercial grade | Manufacturer          |
|------------|------------------|-----------------------|
| LLDPE      | 1001KW           | Exxon Mobil           |
| LDPE       | Q210             | SINOPEC               |
| LLDPE      | Recycled 1001KW/1002KW/1018FA… | Exxon Mobil |
| LLDPE      | Recycled         | Xiongxian, Hebei Province |
| LDPE       | Recycled         | Suning, Hebei Province |

2.2 Material reprocessing. Before the mechanical recycling process, virgin and recycled polyethylene should be put in an oven at 60°C for 4h in order to avoid hydrolysis reactions. Then high-speed commixture of adulterated post-consumer PE was needed in order to make virgin and post-consumer ones mixed homogeneously. Subsequent reprocessing was performed by using a CTE35 twin-screw extruder with 35mm diameter and a L/D ratio of 44(CKC, Nanjing). The temperature profile used was 160, 210, 211, 216, 219, 220, 220, 220, 220 and 220°C. The die temperature was controlled to be 210°C.

3. Results and Discussion

3.1 MFI analysis. Fig.1 depicted the melt flow indices of LLDPE and LDPE with different doping contents. The reclaimed LLDPE were chosen from the Xiongxian city. It was observed that both MFI of PE increased with the increasing adulteration, which indicated the rise of processability. As shown in Fig.1, a predominant reaction of chain scission had occurred in the thermal-mechanic degradation, which resulted from poor free radicals’ recombination in the blend of virgin PE and post-consumer ones.
3.2 Thermo-gravimetric analysis. The TG curves of LLDPE with different doping content were shown in Fig.2. The reclaimed LLDPE was chosen from the Xiongxiang city. It had been suggested that the virgin LLDPE had excellent thermal properties due to the high decomposition temperature, while the thermal temperature had a decreasing tendency with the increasing doping content, which was much lower than virgin LLDPE.
The results indicated virgin LLDPE had better thermal stability due to its single structure. However, the ingredient of the post-consumer LLDPE was prone to be complicated when they suffered from reprocessing, reserve and daily-use. Therefore there existed an adverse effect on the thermal stability of the ones which adulterated with post-consumer polyethylene ones.

3.3 DSC Analysis. The melting temperature ($T_m$) of virgin LDPE and the recycled LDPE with doping was illustrated in Fig.3. The reclaimed LDPE was chosen from the Suning city. As shown in Fig.3, the melting temperature of virgin LDPE was $111^\circ C$. After adulterating post-consumer LDPE, the melting peak had no effective variation, but the melting temperature decreased. From the perspective of thermodynamics, when the temperature of polyethylene got to the melting temperature, the crystalline phase and amorphous phase reached to thermodynamic equilibrium. The melting temperature was calculated by using the relationship:

$$T_m = \frac{\Delta H}{\Delta S}$$

where $\Delta H$ was related to the strength of molecular force; $\Delta S$ was related to the flexibility of molecular chain.

Due to suffering from high temperature and high shear force, the molecular chain of recycled LDPE with doping cracked, and the intermolecular forces receded, which made $\Delta H$ decreased. This was the one reason that resulted in the decrease of melting temperature. The other reason is that the backbone of LDPE which doped with post-consumer LDPE had breakage. The recombination of free radicals made the symmetry and the regularity of molecular chain destroyed. $\Delta S$ had an increasing tendency so that the melting temperature decreased.

![Fig.3 DSC curve of LDPE with different doping contents](image)

The variation of melting peaks of virgin LLDPE and the recycled LLDPE with doping was shown in Fig.4. The post-consumer LLDPE in Fig.4 (a) was from Xiongxian City, and the other post-consumer LLDPE in Fig.4 (b) was from the Exxon Mobile. As can be seen in Fig.4, the virgin LLDPE had only single melting peak and the width of the peak was narrow. After doping with different proportion of post-consumer LLDPE, the heat flow had a distinctly variation, and widen or bimodal peak had appeared. The result showed that the structure of LLDPE with adulterating reclaimed LLDPE was no longer single. Because of complicated ingredient of post-consumer LLDPE and kinds of factors after reprocessing, the molecular chain cracked and the molecular structure varied. The polydispersity
increased which resulted in the variation of melting peak of the LLDPE with doping post-consumer LLDPE.

![DSC curve of LDPE with different doping contents](image)

**Fig.4 DSC curve of LDPE with different doping contents**

4. **Conclusion**

In summary, due to the sophistication of the ingredient of post-consumer PE, the simplicity of the molecular structure of PE materials which adulterated different proportion of reclaimed PE was poor. The MFI increased along with the increasing doping content, which illustrated the improved processing fluidity and the decreased molecular weight. The thermal degradation temperature of adulterated post-consumer PE decreased slightly in comparison with virgin ones. Besides, after adulteration of reclaimed PE, the melting peak had a significant variation: recycled LLDPE appeared bimodal or widened melting peak. The melting temperature of recycled LDPE decreased with the increasing of the doping content of reclaimed LDPE.

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