The Effects of the Recycled Polyethylene on the Properties of Special Material Blends for Pipe and Final Products

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Abstract. A detail comparison between recycled polyethylene (RPE) compounds and special material for pipe in respects of mechanical properties, antioxidant performance, metal contents and rheological behaviours was performed. The results showed that the MFR, the content of ash and typical metallic element of blends increased with the RPE component, while the OIT, fracture strain and impact strength tend to decrease. However, for those unused waste PE there’s no significant difference in most performance parameters compared with the new ones, especially when the RPE content was lower. In contrast, the content of typical metallic element such as Ferrum (Fe) and Calcium (Ca) can still be a crucial indicator for distinguishing the existence of RPE. Undoubtedly, the test of pipe products proved that the introduction of RPE caused the decrease of pressure resistance and resistance to slow cracking.

Keywords. Recycled polyethylene, blends, pipe, metallic element, mechanical properties.

1. Introduction
Each section of polyolefin industrial chain such as production, synthesis, molding, circulation or consumption can generate wastes [1]. Statistically, the annual consumption of global polyolefin products has already been above 100 million tons [2]. The resulting plastic wastes which were difficult to be degraded had become an urgent environmental problem [3]. Taken the year 2017 as a demarcation line, the plastic wastes import prohibition laws which had been enacted by many developing countries have promoted more countries to participate in the wastes recycling. It played active roles in reducing consumption of nature resource [4]. However, the sudden increase of plastic wastes brought huge cost pressure in some developed countries. The lack of international standards in recycled plastics cannot regulate the quality of the recycled blends either. Therefore, in order to avoid quality risks of recycled plastics when manufacturer attempted to reduce those costs, it is necessary to develop identification technique of recycled plastics based on the condition of respective country [5].

Unlike those consumer plastics with short life cycle (ca 1 month to 2 years), polyolefin pipes are usually designed for a long lifetime (more than 50 years) in both industrial and civil field [6]. In other word, the related pipes should be produced with high quality and relative low price. For example, a PE100 pipe has outstanding resistance against pressure and stress cracking, meanwhile, the thinner walls brought the transportation expenses down. What’s more, numerous large enterprises have joined the PE100+ Association, thus expanding their business all over the world. This wide acceptance of PE compounds results from (1) a high level specifications imposed by International Standards Organisation who developed ISO 4437 and ISO 4427 for PE gas and water pipes respectively; (2) the high recycle rate during the molding process and the old pipelines update process. In these two steps, ‘in-plant’ recycling and mechanical recycling are two major recycle techniques [7]. Compare with the...
un-degradation plastic scrap in manufacturing process, the RPE after use which have lost their mechanical properties in some extent were not allowed to reuse in the same pressure application [8].

At present, the application of degradable plastics was still restricted by the high costs. It would be reasonable to believe that the polyolefins would maintain higher market occupancy for a long while in worldwide markets. Thus, a thorough study of recycled plastics has a realistic importance to not only alleviate the economic and environmental pressures but use them correctly. In this work, we have examined how the presence of RPE affects the properties of both special material for pipe in their blends and final pipe products, which is closed related to the continuous development of the whole recycled plastics industry.

2. Experimental

2.1. Materials
The special materials for PE100 pipe (W1 (TUB121N3000B), W2 (JHMGCl00S), W3 (HE3490LS) and W4 (P6006)) are commercially available from Dushanzi Petrochemical Company, Jilin Petrochemical Company, Bolu Chemical and Saber Basic Industries Corporation, respectively. In order to make the reclaimed materials representative, the recycled materials (R1, R2, R3) used in this experiment were collected from markets in different provinces of China.

2.2. Material Preparation and Processing
The proportion of four different PE-RPE compounds (95/5, 90/10,70/30, 50/50, wt/wt%) were extruded at 190-230°C of barrel temperature profile. Similarly, the extrusion step of composition pipes was as follows: one kind of PE pipe material and two kinds of RPE were mixed in different proportions and extruded for pipe DN110 and DN32 by a tube extruder. The process conditions of the pipe preparation are shown in table 1, the traction rate of DN110 pipe production is 1.57 m/min, and that of DN32 pipe production is 15.45 m/min. The process conditions of the pipes were listed in table 1.

| Table 1. The process conditions of the pipes. |
|---------------------------------------------|
| Baiting Cylinders | Head |
| E1.1 | E1.1 | E1.2 | E1.3 | E1.4 | E1.1 | E1.2 | E1.3 | E1.4 | E1.5 | E1.6 | E1.7 | E1.8 |
| Temperature (°C) | 32 | 189 | 189 | 187 | 190 | 190 | 196 | 199 | 200 | 200 | 200 | 232 |

2.3. Characterization
The melt flow rate is measured by a melt flow rate meter. The content of metal elements was measured by an inductively coupled plasma emission spectrometer. The tensile properties were tested according to GB/T 1040.2-2006, the tensile rate was 50 mm/min. The oxidation induction time was tested by DSC according to GB/T 19466.6-2009. Evaluation of slow cracking performance was conducted according to GB/T 18476-2001 by a hydrostatic testing machine.

3. Results and Discussion
Table 2 compared the properties between three kinds of commercial RPE and four virgin materials. It can be seen that the all RPE had much higher melt flow rate (MFR) and the ash content, but a lower oxidation induction time (OIT), which were closely related to their in-service use and reprocessing histories. Previous work had proved that the polyolefins reclaimed after use must have been degradation caused by oxidation, represent by chain scission, recombination, and decrease in molecular weight [9]. Also, the remaining contaminant or the additives introduced more impurities in the RPE materials. Generally, the ash content of the virgin material of the pipe is below 0.08%. According to the result of ash content, it is predicted that the RPE should have more metal elements either. Therefore, the metal element contents in RPE and virgin ones were analyzed by Inductively
Coupled Plasma Atomic Emission Spectrometer (ICP-AES). The results clearly show that the RPE indeed had higher content of various metal elements, and the content of iron (Fe) and calcium (Ca) in the RPE were particularly significant beyond the virgin ones, which have been reached to 100 ppm and 300 ppm, respectively. When the RPE was of poor quality, the maximum value of typical metal elements can reach hundreds of times higher than standard.

Table 2. Melt index, antioxidant properties, ash content as well as elemental analysis of virgin and recycled materials.

| Sample | MFR (g/10 min) | OIT (min) | Ash content (%) | Metal elements content (ppm) |
|--------|----------------|-----------|----------------|-----------------------------|
|        | 5 kg | 21.6 | 210 °C | 200 °C | 850 °C | Fe | Ni | Ca | Na | Mg | K | Ti | Mo | Zn | Cu |
| W1     | 0.28 | 8.3 | 50.8 | 134.4 | 0.0627 | 1.08 | / | 87.5 | 17.43 | 5.55 | 3.97 | 2.42 | / | 0.49 | / |
| W2     | 0.24 | 7.7 | 63.3 | 153.4 | 0.0287 | 0.58 | / | 69.7 | 18.99 | 8.11 | 4.91 | / | / | 52.45 | / |
| W3     | 0.24 | 7.8 | 42.6 | 94.9 | 0.0526 | 2.9 | 0.2 | 115.8 | 8.1 | / | 5.8 | 3.0 | 0.1 | 2.2 | / |
| W4     | 0.24 | 7.0 | 68.0 | 150.5 | 0.05 | 4.4 | / | 66.8 | 8.4 | 0.8 | 9.5 | 3.1 | 0.1 | 60.8 | / |
| R1     | 0.36 | 10.0 | 17.4 | 63.6 | 0.136 | 119.2 | / | 313.4 | 31.3 | 30.7 | 10.2 | 5.6 | 0.2 | 50.2 | 11.0 |
| R2     | 2.56 | 41.0 | 3.7 | 0 | 3.205 | 533.3 | 0.1 | 934.5 | 35.6 | 202.4 | 104.2 | 44.6 | 0.3 | 81.5 | 40.8 |
| R3     | 1.44 | 25.7 | 6.3 | 11.8 | 2.650 | 164.2 | 0.5 | 10550 | 16.6 | 347.9 | 29.6 | 267.4 | 1.0 | 76.3 | 20.7 |

Base on the above analysis, we further examined the influence of the presence of RPE to the properties of PE-RPE blends (PRB). The R1 and R3 were chosen to melt blend with W2 and extruded to prepare PRB in different proportions. The RPE samples were selected according to the boundary method. As the performance of R1 was similar to virgin ones while R3’s metal elements were up to many times the standard limit. It’s well known that the rheological test has a sensitive response to the structural changes of the polymer material and is considered to be an extremely effective method for characterizing the structure and performance of multiphase/multicomponent polymer systems [10]. We thus investigated the rheological behaviour of the PRB system. Figure 1 show the store modulus (G’) and the loss modulus (G”) curve through the dynamic frequency sweeping. For PRB1 (W2/R1), there was no obvious differences among the compounds with different proportions although the RPE and virgin ones could be easily distinguished. In contrast, the PRB2 (70/30, 50/50) were easily distinguishable and the more R2 that PRB2 have, the less G’ it exhibited in the high-frequency, which can be attributed to the increasing degradation level.

For PRB in different proportions, the physicochemical and mechanical properties were also listed in table 3. Interestingly, it is likely to draw the wrong conclusions when we used the simplest method such as MFR and ash content to judge the unknown samples (PE or RPE). Because the criteria based on these parameters were correct only in certain situations. For instance, the MFR of both PRB were between 0.2 and 0.3, which is within the allowable range of the MFR standard of the pipe special material. Similarly, the ash content of PRB1 (70/30) was only 0.066%, which was also correspond with some virgin ones. On the other hand, the OIT, Nominal tensile strain at break (NTSB) and impact strength (IS) demonstrated a regularly drop when the RPE content raised, indicating the inevitable decrease of special material performance after blending the RPE. Besides, it is confirmed that the contaminant and the additives in RPE remain in the resultant compounds, which made ICP-AES method an effective way to determine the recycled polyolefins.
Figure 1. Rheological curves of samples with different content of R1 and R2: (a) PRB1, G’ (b) PRB1, G" (c) PRB2, G’ (d) PRB2, G”.

Table 3. Specific parameters of samples with different content of RPE.

| Sample       | MFR (g/10 min) | OIT (min) | Ash content (%) | Fe (ppm) | Ca (ppm) | NTSB (%) | IS (23°C, KJ/m²) |
|--------------|----------------|-----------|-----------------|----------|----------|-----------|-----------------|
| PRB1 (95/5) | 0.21           | 36.8      | 0.035           | 5.8      | 86.9     | 670       | P23             |
| PRB1 (90/10)| 0.22           | 31.1      | 0.041           | 10.6     | 98.6     | 640       | P23             |
| PRB1 (70/30)| 0.24           | 19.2      | 0.066           | 27.2     | 132.2    | 560       | P21             |
| PRB1 (50/50)| 0.28           | 26.9      | 0.089           | 51.8     | 178.3    | 540       | P18             |
| PRB2 (95/5) | 0.22           | 41.5      | 0.126           | 7.8      | 524.6    | 480       | P21             |
| PRB2 (90/10)| 0.22           | 30.8      | 0.229           | 15.2     | 1004.3   | 500       | P19             |
| PRB2 (70/30)| 0.25           | 24.5      | 0.658           | 44.9     | 2785.0   | 430       | P14             |
| PRB2 (50/50)| 0.30           | 17.8      | 1.052           | 72.3     | 4686.0   | 370       | P11             |

To avoid the degraded RPE reusing in the pressure application, we attempted to extrude the above PRB for demonstrating the damage of the incorrect recycling ways (table 4). Compared with the pipes made of new materials, the inner and outer surfaces of pipes made of PRB were usually rough, which made the extrusion processing more difficult since the melt fracture would be more likely to occur. This will bring a series of problems such as the surface quality of the pipe. Meanwhile, the lower OIT reflected the poor thermostability of the pipes. More important, the addition of RPE would adversely affect the pressure and slow crack growth (SCG) resistance of pipe products [11, 12]. For R1, when the addition amount exceeded 10%, the hydrostatic strength at 20 °C was significantly reduced. When the addition amount reached to 30%, the hydrostatic test was only maintained for 79.77h accompany with the breaking and failure. However, the hydrostatic test at 80 °C all exceeded 1000h. For R2, even a little addition would cause a significant reduction in the pressure resistance of the pipe product and the fracture failure occurred 120.43h later. When the R2 addition amount reaches to 30%, the hydrostatic strength at 80 °C also decreased sharply. Otherwise, no matter which grade of RPE was added, the SCG resistance of the pipe would be reduced, which affected its long-term service life. Under the same proportion, the performance attenuation caused by the R2 is higher than that caused by R1.
Table 4. MFR, OIT and mechanical properties of pipes with different content of RPE.

| Sample | MFR (g/10 min) | OIT (min) | Elongation at break (%) | Hydrostatic strength (20 °C, 12.4 MPa) | Rupture time (h) | SCG (h) |
|--------|----------------|-----------|--------------------------|--------------------------------------|-----------------|---------|
|        |                | 210 °C 50 mm/min | 20 °C, 12.4 MPa | 80 °C, 5.5 MPa | 80 °C, 0.92 MPa |          |
| SCG    | 5 kg           |           |                          |                                      |                 |         |
| PRB1 (95/5) | 0.23         | 31.3      | 568                      | 463.99                               | >1274.42        | 406.48  |
| PRB1 (90/10) | 0.24         | 40.9      | 580                      | 268.69                               | >1274.42        | 369.45  |
| PRB7 (70/30) | 0.27         | 23.0      | 578                      | 79.77                                | >1283           | 297.77  |
| PRB7 (50/50) | 0.30         | 22.1      | 605                      | 57.87                                | >1283           | 280.58  |
| PRB1 (95/5) | 0.28         | 23        | 567                      | 170.16                               | >1274.19        | 233.00  |
| PRB1 (90/10) | 0.25         | 39.7      | 566                      | 120.43                               | >1274.19        | 190.97  |
| PRB1 (70/30) | 0.36         | 8.3       | 581                      | 154.8                                | >1283           | 61.73   |
| PRB1 (50/50) | 0.58         | 0         | 524                      | 66.75                                | 79.65           | 6.23    |

4. Conclusion

In this work, through the investigation of mechanical properties, antioxidant performance, metal contents and rheological behaviours to PE special material for pipe, RPE, PRB and pipe products, we have found a facile strategy to identify the RPE by evaluating the content of Fe and Ca. Then, we strongly recommend that such degradation wastes should be recycled into those were less mechanically demanding. Because the reuse of waste plastics could be accompanied by a negative influence on mechanical properties such as pressure and SCG resistance. To sum up, we should take a rigorous and standard attitude to develop the recycling plastic industry in the perspective of national energy security.

Acknowledgments

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