Research Article

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Preparation and properties of metal textured polypropylene composites with low odor and low VOC

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Abstract: The aim of the present work is to upgrade the functionality and environmental friendliness of polypropylene (PP) by means of a blending technique. The influence of the metal pigment on the odor, volatile organic compounds (VOC) and metal texture of PP, and the effects of the extractant, adsorbent and processing technology on the odor and VOC of PP composites were studied systematically. It was found that metallic pigment significantly increased the VOC, odor, metallic texture and MFR of PP, and reduced the impact strength and elongation at break. The adsorbent and extractant can effectively reduce the VOC and odor of the PP composites. When the adsorbent and extractant contents were 0.5 and 5 wt%, respectively, the maximum reduction in the VOC and odor reached 73.6% and 1 level, respectively. When the extractant and adsorbent were used at the same time, the method of adding extractant and adsorbent from the main and the secondary feeding port respectively was significantly superior to the method of adding the extractant and adsorbent from the main feeding port together in reducing the odor and VOC of PP composites, which displayed a good synergistic effect.

Keywords: extractant; adsorbent; metallic pigments; processing technology

1 Introduction

Polypropylene (PP) is widely used because of its good performance and low cost. However, in the whole life cycle of PP, low molecular volatile compounds are produced, such as those generated due to an incomplete reaction and incomplete solvent removal during the synthesis process and degradation during the fabrication process and use. In addition, additives or materials containing a large amount of low molecular volatiles are introduced to obtain high performance, and paint is introduced to increase the adhesive properties in the latter surface treatment of the product, which can lead to a high amount of volatile organic compounds (VOC) in the PP and its products [1–3]. VOC contains a large number of toxic and harmful substances, such as alkanes, aromatics, olefins, esters, aldehydes, and ketones, which are volatile at room temperature. Long term inhalation will bring serious harm to human health. High amounts of VOC and odor will limit the application of PP products in relatively enclosed environments, such as automobiles, home appliances and furniture [4].

Over the past few decades, many researchers have carried out considerable research on VOC composition, low VOC treatment technology and spray-free treatment technology for the preparation of polymers, obtaining some good results in these fields of research. Some researchers used GC–MS, dynamic dilution olfactometry and field of odors method – to identify low molecular weight compounds and odor [5–13]. Some researchers investigated the adsorption mechanisms of VOCs on porous polymeric resin, their odor formation mechanisms and the effects of the adsorbent on the VOCs and odor [14–24]. Some researchers investigated the effect of processing technology on the VOC and odor [25, 26]. Some researchers realized surface metallization of plastics using a grafting method and laser induced method [27–29]. Metal textured plastic is an important development direction of spray-free technology, which not only improves the qualification rate, but also eliminates the need for a later surface treatment step.
Metal textured plastics are usually prepared by adding a metallic pigment into the plastic matrix. The carrier of the metal pigment contains a large amount of low molecular volatile compounds, which will lead to a higher amount of VOC and odor in the prepared metal textured plastics. In order to be widely used, metal textured plastics must be treated with low odor and low VOC. At present, there are few studies on metal textured plastic. In particular, the effects of metal pigments on the odor, VOC and metal texture of plastic have rarely been reported to date to the best of our knowledge.

In these previous studies, the individual effects of the processing technology, extractant and adsorbent, or, at most, a combination of two of them, were considered [14, 21, 24, 26]. Recently, we focused our research on metal textured plastics and the combined effects of the processing technology, extractant and adsorbent on the VOC and odor, and obtained a very effective way to prepare polymer composites with low odor and low VOC. In this work, we used two kinds of metal pigments to study the influence of carrier on the odor, VOC, metal texture and mechanical properties of PP. The combined effects of the processing technology, extractant and adsorbent on the odor and VOC of PP/metal pigment composites have been studied in order to reduce the total amount of VOC and slow down the escape rate of residual low-molecular volatile compounds to the greatest extent, and obtain metal-textured, environmentally friendly and recyclable PP composites.

2 Experimental

2.1 Materials

PP (propylene-ethylene copolymer, 7926) was supplied as pellets by Shanghai SECCO Petrochemical Company Limited, China. The extractant (BYK4200) was supplied by BYK Chemie, Germany. Antioxidants 1010 and 168 were supplied by Ciba Specialty Chemicals Inc., Switzerland. Adsorbent XC01 was supplied by Ma’anshan Keli Chemical Technology Co., Ltd., China. Metallic pigment A (MPA, PE3001) and B (MPB, AL1401MO) were obtained from Shanghai FulColor Advanced Material Co., Ltd., China.

Table 1: Data for the two kinds of metallic pigment used.

|                | MPA     | MPB     |
|----------------|---------|---------|
| Carrier        | PE wax  | White oil |
| Aluminum content/wt% | ~70     | ~70     |
| Aluminum particle size (D50)/µm | 30      | 14      |
| Aluminum particle shape | Flake   | Flake   |
| VOC/(µg·g⁻¹)  | 6570.7  | –*¹     |
| Odor level     | 4.5     | 5.5     |
| Volatility/(wt%)*²| 0.092   | 0.466   |

*¹ – Fail to test according to VDA278, *² – Test conditions, 90°C × 0.5 h.

Scheme 1: A schematic representation of the preparation process adding the adsorbent and extractant separately.
Data for the two kinds of metallic pigment are listed in Table 1.

2.2 Specimen preparation

One or more of the metallic pigment and the extractant were mixed with PP and the antioxidant in a high-speed kneader (SHR-100, Zhangjiagang Yili Machinery Co., Ltd, China). The mixture was extruded in a co-rotating twin screw extruder (SHJ-36B, Nanjing Hongming extrusion equipment Co., Ltd, China). Wherein antioxidants 1010 and 168 were both 0.2 phr. The temperature of each section of the extruder was 180°C (60°C), 190°C (70°C), 190°C (80°C), 190°C, 200°C, 200°C, 210°C, 220°C, 220°C, 210°C and 210°C from the main feeding port to the die head, as shown in Scheme 1. The temperature in the brackets was selected when an extractant was used. When using the adsorbent, if there were no special instructions, it was added from the secondary feeding port alone and the other materials were added from the main feeding port. The screw speed was 300 r/min, the vacuum was −0.08 MPa and the obtained pellets were molded into dumbbell-shaped tensile bars (GB1040 type II specimens, 150 × 10 × 4 mm), V shaped notch impact test bars (GB1843, 63.5 × 10 × 4 mm, tip radius = 0.25 mm, depth = 2 mm), metal texture test sample and odor test sample (100 × 100 × 5 mm) using a HDX50 machine (Ningbo Haida Plastic Machinery Co., Ltd, China).

2.3 Mechanical properties test

The tensile properties were measured using a MTS universal testing machine (Model CMT4204) at room temperature. The tensile tests were characterized at a crosshead speed of 50 mm/min. A notched Izod Impact strength test was performed at a rate of 3.5m/s on a ZBC1400B impact test machine (MTS Systems Corporation) at room temperature. The reported values are the average of five individual measurements.

2.4 Melt flow rate test

The melt flow rate (MFR) was measured at 230°C under a 2.16 kg load using a ZRZ400 melt flow index test machine (MTS Systems Corporation). The reported values are the average of five individual measurements.

2.5 Odor analysis

The odor was measured according to VDA 270. The evaluation criteria for odor were shown in Table 2. The sample volume was 50 cm³ and the container volume was 1 L. The storage temperature was 80°C and the storage duration was 2 h. Experiments were carried out by five testers. The odor characteristics were indicated as an arithmetic mean of the individual grades, the value being rounded to half-step grades.

Table 2: Evaluation criteria for odor.

| Odor level | Odor characteristics          |
|------------|-------------------------------|
| Grade 1    | Not perceptible               |
| Grade 2    | Perceptible, not disturbing    |
| Grade 3    | Clearly perceptible, but not disturbing |
| Grade 4    | Disturbing                    |
| Grade 5    | Strongly disturbing           |
| Grade 6    | Not acceptable                |

2.6 VOC analysis

The VOC was measured according to VDA 278 using a TDS-GC/MS apparatus (TDS3, Gerstel, Inc., GER. GC/MS7890B/5977B, Agilent Technologies Ltd., USA). The sample consists of 60 g of the PP composite pellets. The sample was heated at 90°C for 30 min under a nitrogen atmosphere. The VOC value was determined using two measurements. The higher value of the measurements was used as the result. The VOC value was the total of the readily volatile to medium volatile substances, and it was calculated as the toluene equivalent.

2.7 Volatility test

The metallic pigment was heated at constant temperature for a specific time in a ventilated oven (Shanghai Laboratory Instrument Works Co., Ltd, China). It was then removed from the ventilated oven and weighed using a Jingke analytical balance Model TG328B at room temperature. The volatility of the metallic pigment was determined by calculating the weight change. The reported values are the average of three individual measurements.
2.8 Characterization of metal texture

The samples were observed using a Canon camera (Model EOS77D). The magnification was 1 times. The scale was calibrated using a Vernier caliper.

2.9 Water absorption rate test

The PP composite pellets were dried to constant weight at 100°C and then placed in the high and low temperature test chamber (HUT-705P, Chongqing Hardy Technology Co., Ltd). The temperature was 23°C and the relative humidity was 50%. After storing for a specific period of time, the sample was weighed. The reported values are the average of three individual measurements. The water absorption rate ($Wm$) was obtained as follows:

$$Wm = \frac{(Mb - Mg)}{Mg} \times 100\%$$

where $Mb$ is the weight after water absorption, $Mg$ is the weight after drying.

3 Results and discussion

3.1 The effects of the metal pigment on the properties of PP

3.1.1 The effects of the metal pigment on the VOC and odor of PP

In order to intuitively reflect the influence of the metallic pigment on pure PP, “0” was used to represent pure PP in Figures 1 and 2. Pure PP was not extruded, but only analyzed and tested upon being injection molded into the standard sample.

Figure 1 shows the effects of the metal pigment on the VOC and odor of the PP. When <1 wt% of metal pigment was used, the VOC and odor in PP decreased. When the metal pigment content was >1 wt%, which increased rapidly upon increasing the metal pigment content. MPB had greater impact and the VOC and odor increased by 148.7% and 1 level, respectively.

This result shows that the metal pigment had a significant effect on the VOC and odor in the PP. The carrier of the metal pigment contains a large amount of low molecular weight volatile compounds, resulting in a high VOC and odor in the PP composites. In addition, the volatility of the white oil used in MPB was higher than that of PE wax (Table 1), which had a greater impact on the VOC and odor of the PP. The mixture of PP and metal pigment was processed using twin screws. Due to the high temperature volatilization and high vacuum extraction steps, the VOC and odor in the PP composites were significantly reduced. Therefore, after blending with a small amount of the metal pigment, the VOC and odor decreased to some extent. Further increasing the metallic pigment content rapidly increased the VOC and odor in the PP composites.

In summary, MPB has a more significant effect on the VOC and odor of PP among the two metallic pigments studied.

3.1.2 The effects of the metal pigment on the mechanical properties and MFR of PP

Figure 2 shows the effects of the metal pigment on the mechanical properties and melt flow rate (MFR) of PP. As shown in Figure 2a, the effects of the two kinds of metal pigments on the tensile strength were small, which decreased upon increasing the metal pigment content. When the metal pigment content reached 10 wt%, the tensile strength decreased by <8%. As shown in Figure 2b, when the metal pigment content was ≤5 wt%, the effects of the two kinds of metal pigments on the elongation at break
were almost equivalent, while when it was >5 wt%, the effect of MPB was larger than that of MPA, in which the higher reduction in the elongation at break was 52.7%. In terms of the impact strength, the effects of the two kinds of metal pigments were significant with the effect of MPA being the largest, which decreased upon increasing its content. When the metal pigment content reached 10 wt%, the largest reduction in the impact strength was observed, which reached 46.4%, as shown in Figure 2c.

The above experimental results show that the metal pigments have little effect on the tensile strength of PP, but have a significant effect on the elongation at break and impact strength. It may be that the aluminium powder in the metallic pigments increases the tensile strength of PP, while the two kinds of carriers may weaken the tensile strength of PP because they are all low strength organic compounds. The results show that the tensile strength decreased upon increasing the metal pigment content. In terms of the elongation at break and impact strength, the aluminium powder and two kinds of carriers can weaken them because the slip between the molecular segments of PP was destroyed. The result of the combined effects was that increasing the metal pigment content rapidly decreases the elongation at break and impact strength of PP.

Figure 2d shows the effects of the metallic pigment on the MFR of PP. It can be seen that the two kinds of metal pigments have little effect on the MFR, which slightly increased upon increasing the metal pigment content. When the content exceeded 3 wt%, the effect of MPB on the MFR of PP significantly increased. When the metallic pigment content reached 10 wt%, the largest increase in the MFR was 26.4%.

It may be seen that the main factors that affect the MFR were the shape, particle size and metal particle content, as well as the type of carrier used. Both carriers were blow melting point organic compounds, which are beneficial toward improving the fluidity of PP. The metal particles were solid with a flake-like morphology, which can weaken the fluidity of PP [30]. The competition between the two factors results in a slight increase in the MFR upon increasing the metal pigment content. Because the carrier content and the shape of the metal particles of the two kinds of metal pigments were the same, the influence of the metal pigments on the MFR mainly depended on the particle size of metal particles and type of carrier used. The smaller the particle size of the metal, the better the fluidity of the carrier, and the more it improves the MFR. The results show that increasing the metal pigment content led to an improvement in the MFR, which was more obvious for MPB.
3.1.3 The effects of the metal pigment on the metallic texture of PP

Figure 3 shows the effects of the metallic pigment on the metallic texture of PP. It can be seen that the two kinds of metal pigments had great effect on the metallic texture. The metallic texture of PP composites significantly increased upon increasing the metal pigment content. When the content reached 5 wt%, the appearance of PP / metal pigment composites was similar to that of pure aluminium. When the content reached 10%, the appearance of PP / MPA composites was very similar to that of pure aluminium, as shown in Figures 3d and 3h. The effect of MPA on the metal texture of PP was greater than that of MPB. This was mainly due to the larger particle size of metal powder in MPA.

Based on the experimental results observed for the odor, VOC, mechanical properties, MFR and metallic texture, the content of the metal pigment was selected to be 5 wt% in our further studies.

3.2 The effects of the adsorbent and extractant on the VOC, odor and water absorption of the PP/metallic pigment composites

3.2.1 The effects of the adsorbent on the VOC and odor of PP /metallic pigment composites

Figure 4 shows the effects of the adsorbent on the VOC and odor of the PP/metal pigment composites. It was clear that upon increasing the content of the adsorbent, the VOC and odor of the PP composites were continuously improved, especially the VOC. When the adsorbent content reached 3 wt%, the VOC of the two PP composites decreased by 71.6 and 35.1%, respectively and the odor of the two PP composites improved from 2.5 to 2.0 and 3.0 to 2.0, respectively. When the content of the adsorbent was >2.0 wt%, the VOC and odor were not obviously improved.

This was attributed to the adsorbent not only exhibiting a strong physical adsorption capacity, but also the ability to decompose or chelate nitrogen hydride, sulfide, car-
bon oxide and other small molecules. When the adsorbent was added to the PP composites, it will not only weaken the volatile ability of the low molecular weight matter in the PP composites, but also reduce the total volatile amount of low molecular weight matter in the PP composites due to its strong physical adsorption and chelation decomposition ability and thus, effectively improve the VOC and odor of the PP composites.

3.2.2 The effects of the extractant on the VOC and odor of the PP /metallic pigment composites

Figure 5 shows the effects of the extractant on the VOC and odor of the PP/metal pigment composites. It can be seen that increasing the content of the extractant continuously improved the VOC and odor of the PP composites, especially the VOC. When the extractant content reached 5 wt%, the VOC of the two PP composites decreased by 64.3 and 59.2%, respectively, and the odor of the two PP composites improved from 2.5 to 2.0 and 3.0 to 2.0, respectively. When the content of the extractant was >2 wt%, the VOC and odor were not obviously improved.

It may be seen that the extractant is a kind of masterbatch with a porous polymer as the carrier and rich in low boiling volatile components. During the preparation of the PP composites, the carrier is softened and releases the low boiling point extractant after being heated. The extractant forms a large number of microbubbles under the action of heat and shear force. The microbubbles are mutually soluble and extracted with VOC, such as alkanes, olefins, aldehydes and ketones, which were evacuated under the action of the negative pressure at the middle of the extruder (Scheme 1). The extractant effectively removes the low molecular weight volatile compounds, thereby effectively reducing the VOC and odor of the PP composites.

3.2.3 The effects of the adsorbent and extractant on the water absorption of the PP /metallic pigment composites

Figure 6 shows the effects of the adsorbent and extractant on the water absorption of the PP/metallic pigment composites. Because the adsorbent is a porous solid powder and has a strong acting force on low molecular weight substances, the composite material formed with it had strong water absorption properties, as shown in Figures 6a and 6b. It was found that increasing the adsorbent content increased the water absorption of the two PP composites. When the adsorbent content reached 1 wt%, the water absorption of the two PP composites increased by 114.5 and 111.5%, respectively after standing for 24 h. Over time, when the standing time reached 720 h, the water absorption of the two PP composites increased by 220.8 and 214.1%, respectively. This phenomenon was more obvious when the adsorbent content was higher. A high water absorption will lead to a reasonable drying treatment step and sealed storage when using the product, thereby increasing its workload in use. If not handled properly, it will seriously affect the appearance and even the performance of the product. Therefore, during the modification process of these PP composites, the recommended amount of the adsorbent used is 0.5 wt%.

Because the extractant was removed after the miscible extraction of the low molecular weight substances in the PP composites was completed and there was little residue in the PP composites, and thereby, have little effect on the water absorption of the PP composites, as shown in Figures 6c and 6d.

Figure 5: The effects of the extractant on the VOC and odor of the PP/metal pigment composites.
3.2.4 The effects of feeding method of the adsorbent and extractant on the VOC and odor of the PP/metallic pigment composites

Based on the adverse effects of the high water absorption of the adsorbent, 0.5 wt% of the adsorbent was selected to be combined with the extractant for further study, as shown in Tables 3 and 4. Upon increasing the extractant content, the VOC and odor of the PP composites were reduced. When the extractant content reached 1.0 wt%, the odor of the PP/MPA composites improved from 2.5 to 2.0 using feeding method A, as shown in Table 3. When the extractant content reached 2.0 wt%, the odor of the PP/MPA composites was also improved from 2.5 to 2.0 using feeding method B.

The PP/MPB composites showed similar results using the different feeding methods, as shown in Table 4. When the extractant content reached 5.0 wt%, the VOC of the PP/MPB composites...
Table 4: The effects of feeding method used for the adsorbent and extractant on the VOC and odor of the PP/MPB composites.

| Adsorbent content /wt% | Extractant content /wt% | VOC/(µg·g⁻¹) Feeding method A | VOC/(µg·g⁻¹) Feeding method B | Odor level Feeding method A | Odor level Feeding method B |
|------------------------|-------------------------|-------------------------------|-------------------------------|-----------------------------|-----------------------------|
|                        |                         |                              |                               |                             |                             |
| 0                      | 0                       | 195.1±9.7                    | 195.1±9.7                    | 3.0±0.27                    | 3.0±0.27                    |
| 0.5                    | 0                       | 179.5±6.8                    | 179.5±6.8                    | 2.5±0.22                    | 2.5±0.22                    |
| 0.5                    | 0.5                     | 156.8±6.4                    | 176.8±4.8                    | 2.5±0.22                    | 2.5±0.22                    |
| 0.5                    | 1.0                     | 128.2±5.7                    | 146.5±2.4                    | 2.5±0.27                    | 2.5±0.27                    |
| 0.5                    | 1.5                     | 93.5±2.9                     | 112.3±3.1                    | 2.0±0.0                     | 2.5±0.20                    |
| 0.5                    | 2.0                     | 68.2±1.8                     | 93.6±2.8                     | 2.0±0.0                     | 2.0±0.22                    |
| 0.5                    | 5.0                     | 51.6±1.1                     | 72.1±1.4                     | 2.0±0.0                     | 2.0±0.0                     |

MPA composites and PP/MPB composites decreased by 73.0 and 73.6%, respectively using feeding method A when compared to the PP/metallic pigment composites prepared without an adsorbent, while they were reduced by 64.7 and 63.0%, respectively when using feeding method B. According to the experimental results obtained for the odor and VOC shown in Tables 3 and 4, it can be seen that feeding method A was obviously superior to feeding method B. At the same time, it is also found that the extractant and adsorbent display a good synergistic effect when using feed method A. The extractant and adsorbent were added separately (Scheme 1), which can give rise to their respective functions and avoid any adverse effects that are difficult to extract due to the adsorption of the adsorbent. The combined use of an adsorbent and extractant can achieve significant improvements even at lower levels.

When feeding method A was used, the VOC in the PP composites can be removed to a large extent after being mutually soluble and extracted with the extractant. Even if there was a small amount of residue present, the volatilization ability of the residual VOC will be weakened due to the strong physical adsorption of the adsorbent. As a result, the odor was effectively improved and the VOC were reduced.

4 Conclusions

During the extrusion process, high temperature and high vacuum can reduce the VOC and odor of PP-based materials. Increasing the metallic pigment content, the VOC, odor, metallic texture and MFR increase rapidly, while the impact strength and elongation at break decrease rapidly. When the metallic pigment content reached 10 wt%, the largest increase in the VOC, odor and MFR of PP was observed and reached 148.7%, 1 level, and 26.4%, respectively, and the largest reduction in the impact strength and the elongation at break observed reaching 46.4 and 52.7%, respectively. Metallic pigment with white oil used as a carrier had a more significant effect on the VOC, odor and MFR when compared to metallic pigment using PE wax as a carrier, but the opposite was true for the impact strength and metallic texture and equivalent in terms of the tensile strength.

The absorbent and extractant can effectively reduce VOC and odor of the PP/metal pigment composites. When the absorbent content reached 3 wt%, the VOC of the two PP composites decreased by 71.6 and 35.1%, respectively, and the odor improved from 2.5 to 2.0 and 3.0 to 2.0, respectively. When the extractant content reached 5 wt%, the VOC of the two PP composites decreased by 64.3 and 59.2%, respectively, and the odor improved from 2.5 to 2.0 and 3.0 to 2.0, respectively. The adsorbent significantly increased the moisture absorption of the PP/metal pigment composites, while the extractant had little effect on the moisture absorption.

When the extractant and adsorbent were used at the same time, the method of adding extractant and adsorbent from the main and the secondary feeding port respectively was superior to the method of adding the extractant and adsorbent from the main feeding port together in reducing the odor and VOC of the PP/metal pigment composites, which displayed a good synergistic effect.

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