PREPARATION OF MASTERBATCH CONTAINING ANTI-OXIDATION ADDITIVE: EFFECT OF CARRIER RESIN RATIO AND ADDITIVES CONTENT

Duong Thi Thao$^1$, Nguyen Phi Trung$^1$, Hoang Thi Huong$^1$, Tran Vu Thang$^2$, Nguyen Van Khoi$^2$,*, Trịnh Đức Công$^2$, Hoang Thi Phương$^2$

$^1$Institute of Research and Development on Novel Materials, 350 Lac Trung, Hai Ba Trung, Hà Nội
$^2$Institute of Chemistry, VAST, 18 Hoàng Quốc Việt, Cầu Giấy, Hà Nội

*Email: khoinguyen56@gmail.com

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ABSTRACT

In this article, we investigated effect of carrier resin ratio and anti-oxidation additives content on properties of anti-oxidant additives Masterbatches (MBs). The characteristics were measured by: melt flow index (MFI), morphology (SEM), tensile strength and elongation at break. The results indicated that: increasing LLDPE content in carrier resin led to decreasing mechanical properties, MFI weren’t uniform in MBs. With 80/20 of LDPE/LLDPE ratio, the tensile strength and elongation at break values were highest (21.0 MPa, 680.5 %). In addition, when increased anti-oxidant additives content, mechanical properties increased to upper limit value, then decreased. With 25 wt.% of anti-oxidant additives, the tensile strength and elongation at break values were highest (21.0 MPa, 654.7 %), MFI were uniform in MBs (12 g/10 m). SEM images were evidence of greatly distribution in sample containing 25 wt.% additives. Consequently, the 90/10 of LDPE/LLDPE ratio, 25 wt.% anti-oxidant additives were selected to prepare MBs.

Keywords: anti-oxidation master batch, carrier resin, LDPE, LLDPE.

1. INTRODUCTION

Plastics industry has important role in our life. Plastics products has many advantages: flexible, good mechanical properties, good resistance to water, acid-base resistance, easy to manufacture various products by different processing, such as: injection molding, extrusion, blow molding, etc. However, in processing and using of products, polymer materials are oxidized, leading to decreasing of performance. To solve this problem, anti-oxidation additives are introduced into polymer matrix [1].

There were many literatures which reported about ability of anti-oxidation additives for different polymer matrix. Jozef Rychlí authority et al. [2] investigated UV resistance ability of polypropylene film incorporating with different additives: Irganox HP 136 and Irganox 1010.
Preparation of masterbatch containing anti-oxidation additive: effect of carrier resin ratio

Characteristics were performed by Fourier Transform Infrared (FT-IR) and carbonyl index. The results showed that Irganox 136 was more effective in anti-oxidation than Irganox 1010. M.J. Galotto et al. [3] studied on anti-oxidation of food packaging containing anti-oxidant additive (Irganox 1076) and evaluated the migration of additive. The experimental results indicated that, Irganox 1076 had good performance in anti-oxidation, there hadn’t migration and influence of additive to food. Hassanpour et al. [4] investigated mechanical properties, the changes in chemical structure, oxidation induction time (OIT) of HDPE/EVA blends containing the synergist of Irganox 1010 and zinc stearate. The results showed that, anti-oxidation ability of samples containing anti-oxidant additive was better than the samples without additive. Many literatures reported that anti-oxidation additives performed effective even using low level of content (0.1 - 0.5 wt.%).

To distribute greatly additives in polymer matrix and decrease dust in processing, additive particles were introduced to polymer matrix by using masterbatch form (masterbatch is a compound of polymer matrix (as carrier resin) and one functional additive, which has low content of polymer and high content of additive). Masterbatch has influence on mechanical properties and dispersion of additives in end-using product. Effective of masterbatch depends strongly on carrier resin and the content of additives. However, there weren’t many researches on carrier resin and content of additives for masterbatch. So, the aim of this paper was to investigate the effect of carrier resin ratio and anti-oxidant additives content on properties of masterbatch samples.

2. EXPERIMENT

2.1. Materials

Low density polyethylene (LDPE) (density: 0.925 g/cm³, MFI = 4 (190°C/2.16 kgf) (supplied by LyondellBasell – Netherland), Linear low - density polyethylene (LLDPE) (density: 0.924 g/cm³, MFI = 21 g/10 min (190°C/2.16 kgf) (supplied by ExxonMobil – USA). Anti-oxidation additives: Irganox 1076 (AO1076), Irganox 168 (AO168), Irganox 1010 (AO1010) were supplied by Tianjin Bestgain Science & Technology – China. Zinc stearate was imported from Singapore. PPA 2800 was supplied by Thanh Loc Chemistry Company – Viet Nam.

2.2. Methods.

2.2.1. Anti-oxidation additive – containing masterbatch preparation

Masterbatch samples were prepared containing the mixture of anti-oxidant agent (Irganox 168/Irganox 1010: 67/33 in weight), carrier resin polyethylene (LDPE, LLDPE), zinc stearate, PPA2800 with calculated amount. Masterbatch samples were blended in Supermix machine for one hour to disperse the components. Well-mixed ingredients were melting mixed in twin-screw extruder (model: BP – 8177 – ZB), the temperature profile: 110-125-130-135-140-140 °C, at a constant rotating speed of 24 rpm). The extrudate was cut in pellets with cylinder shape, uniform in size.

The masterbatch samples include: 20 % anti-oxidant additives, 1 % PAA 2800, 2 % zinc stearate and carrier resin LDPE/LLDPE with different ratios of 90/10 ÷10/90, which have been designated as CT1 ÷ CT9, respectively. Other samples fixed the carrier resin (LDPE/LLDPE:
20/80) and changed the amount of anti-oxidant additives in the range of 15 - 30, which have been designated as MB15, MB20, MB25 and MB30, respectively.

2.2.2. Determination of Melt Flow Index (MFI)

Melt flow index (MFI) of samples were measured by using BP-8164-A instrument, according to ASTM D 1238 and ISO 1133 standard.

2.2.3. Mechanical measurements

The mechanical measurements, including tensile and elongation at break properties of film samples were performed using a tensile tester (Instron 5980), according to ASTM D 638.

2.2.4. Scanning Electronic Microscopy (SEM)

The surface morphology of samples were obtained using Scanning Electron Microscope (SEM) JEOL 6390 instrument in Institute of Materials Science – VAST. The samples were cryogenically fractured in liquid nitrogen and the fracture surfaces were coated with a thin layer of platinium.

3. RESULTS AND DISCUSSION

3.1. Effect of carrier resin ratio on properties of anti-oxidant additive masterbatch

Carrier resin ratio affected to properties of samples characterized by mechanical properties and melt flow index.

Mechanical properties

Effect of component ratio in carrier resin on mechanical properties of masterbatch samples are described in Table 1.

| Sample  | LDPE/LLDPE Ratio | Tensile strength at break (MPa) | Elongation at break (%) |
|---------|------------------|---------------------------------|------------------------|
| CT1     | 100/0            | 18.57                           | 670.5                  |
| CT2     | 90/10            | 21.0                            | 680.5                  |
| CT3     | 80/20            | 20.5                            | 675.4                  |
| CT4     | 70/30            | 20.2                            | 673.4                  |
| CT5     | 60/40            | 19.5                            | 671.2                  |
| CT6     | 50/50            | 19.1                            | 670.8                  |
| CT7     | 40/60            | 18.6                            | 670.1                  |
| CT8     | 30/70            | 17.3                            | 620.4                  |
| CT9     | 20/80            | 16.2                            | 580.4                  |
| CT10    | 10/90            | 15.3                            | 540.1                  |
| CT11    | 0/100            | 14.2                            | 520.3                  |
Preparation of masterbatch containing anti-oxidation additive: effect of carrier resin ratio …

The results showed that when LLDPE content was increased in the carrier resin the mechanical properties of the sample decreased. When LLDPE content increased from 10 to 100 phr, the tensile strength at break decreased from 21.0 MPa to 15.3 MPa, the elongation at break decreased from 680.5 % to 540.1 %. However, with the ratio LDPE/LLDPE CT1-CT7, the mechanical properties were changed less significantly. These results are consistent with those of Nilesh Savargaonkar [5].

*Melt Flow index (MFI)*

Effect of carrier resin ratio on melt flow index of masterbatch samples are showed in Figure 1.

*Figure 1. Effect of carrier resin ratio on melt flow index of masterbatch samples.*

The results showed that CT1, CT2 samples had uniform MFI after 5 measurements. However, the MFI of other samples (CT3-CT11) were not uniform, this phenomenon can be explained by the not greatly dispersion of additives in matrix and these results were suitable with mechanical properties. Therefore, the ratio 80/20 of LDPE/LLDPE was selected for preparation of masterbatch.

3.2. Effects of anti-oxidation additives content on properties of masterbatch

Anti-oxidation additives content effect on properties of samples were characterized by MFI, fractured surface morphology and mechanical properties of sample.

*Mechanical properties*

*Table 2. Effect of anti-oxidation content on mechanical properties of samples.*

| Sample | Anti-oxidation additives content, (%) | Tensile strength at break, (Mpa) | Elongation at break, (%) |
|--------|--------------------------------------|---------------------------------|-------------------------|
| MB15   | 15                                   | 19.05                           | 650.1                   |
| MB20   | 20                                   | 20.5                            | 653.2                   |
| MB25   | 25                                   | 21.0                            | 654.7                   |
| MB30   | 30                                   | 17.6                            | 580.6                   |

59
The effect of anti-oxidation additives content on mechanical properties of sample was investigated. The results are presented in Table 2.

The tensile strength at break and elongation at break values were increased lightly when additives content increased from 20 to 25 wt.% and decreased significantly when additives content increased from 25 to 30 wt.%. These results can be explained so that: additives had a role as reinforcement for polymer matrix, so increasing additives content led to increasing stiffness, tensile strength, elongation. However, when increased additives content over suitable value led to aggregation of additive particles in polymer matrix, led to fracturing at aggregation when samples loaded tensile strength.

*Melt Flow index (MFI)*

The results of melt flow index of the masterbatch containing different anti-oxidation additives content are presented in Table 3.

| Sign | Additives Content (%) | MFI (g/10 m) | External shape |
|------|-----------------------|--------------|----------------|
| MB15 | 15                    | 9.8          | MB granulates had white color, dispersion of additive was not uniform |
| MB20 | 20                    | 11.2         | MB granulates had white color, additives dispersion was fine |
| MB25 | 25                    | 12.0         | MB granulates had white color and additive dispersed finely |
| MB30 | 30                    | 13.5         | MB granulates had white color, dispersion of additive was not uniform |

The MFI results of the masterbatch showed that when increased anti-oxidation additives content, MFI of master batch increased. This can be explained that, Irganox 1010 and Irganox 168 has a short molecular chain when mixed, intermixing between plastic molecules, so increasing the content of additives add to increase the flow index masterbatch.

To evaluate the compatibility between additives and matrix and the dispersion of additives, we determined MFI of MBs containing different additives content 5 times for each sample. The results were shown in Figure 2.

*Figure 2. MFI of MBs in 5 times of measurement.*
When additives content increased from 15 to 25 wt%, leading to increasing of MFI, and MFI were uniform after 5 measurements. When additives content was 30 wt%, MFI weren’t uniform after 5 measurements. These results are explained so that, the increasing additives content overcome a suitable value led to agglomeration of additive particles and the distribution wasn’t finely, so MFI weren’t uniform. Other properties of MBs are presented in Table 4.

Table 4. Moisture and size of MB granulates containing anti-oxidation additives.

| Sign  | Additives Content (%) | Moisture (%) | Size |
|-------|-----------------------|--------------|------|
|       |                       |              | Length (mm) | Diameter (mm) |
| MB15  | 15                    | 0.23         | 0.23 | 3.6 |
| MB20  | 20                    | 0.32         | 0.2  | 3.03 |
| MB25  | 25                    | 0.35         | 0.5  | 3.02 |
| MB30  | 30                    | 0.51         | 0.51 | 3.8 |

The results show that an increasing of additives content (from 15 to 30 wt.%) led to increasing the moisture of MBs (from 0.23 to 0.51 wt.%, respectively). This can be explained by the fact that Irganox 1010 and Irganox 168 contain hydroxyl groups in their molecular, these hydroxyl groups absorbed moisture in air, leading to increasing the moisture content of MBs.

Surface morphology

The surface morphology of the samples are showed in Figure 3.

Figure 3. Surface morphology of the sample containing different additives content.
The obtained SEM images indicate that the dispersion of additives in carrier resin of MB15, MB20, MB25 were greater than MB30 sample. In SEM image of MB30, there is a presence of particles agglomeration, this phenomenon is due to increasing of additives content to overcome a certain value, leading to agglomeration of excess additives. The sample MB 25 which contains 25 wt% anti-oxidants gave the best dispersion of additives, that is suitable with the uniform MFI after 5 measurements and mechanical properties of samples. In addition, the moisture of MB25 was 0.35 wt.%, lower than 0.5 wt.% which is limit moisture for film products. Therefore, 25 wt.% of anti-oxidation content was selected for manufacturing of anti-oxidant additive masterbatch.

4. CONCLUSION

This paper discusses the effect of carrier resin ratio and anti-oxidant additives content on properties of anti-oxidant additives masterbatch. The carrier resin component has significant influence on MFI and mechanical properties of MB samples. In addition, anti-oxidant additives content has influence on MFI, mechanical and morphology of MB samples. The result showed that the component to prepare the anti-oxidation masterbatch includes: PPA 0.5 wt.%, zinc stearate 2 wt.%, LDPE (MFI=2)/LLDPE (MFI=21) (with 90/10 of ratio) 72.5 wt.% and combination of Irganox168/Irganox 1010 (with 70/30 of ratio) with the content from 20 - 25 %.

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