Preparation of laser markable polyamide compounds

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Abstract. Laser marking technique has been increasingly used in electrical and electronic industry in the recent decades for scanning and control purpose. Laser marking is superior to the traditional labelling techniques in terms of speed, flexibility and duration. The mechanism of laser marking is either blackening by carbonization or brightening by microbubbles, upon the effect of laser on the base. Normally laser marking additives were introduced in order to achieve the controllable marking effect. In this paper, a light-on-dark laser markable polyamide compound was studied with the leveraged properties of mechanical, physical and laser marking effect.

Keywords: Laser Marking; Polyamide; Compounds

1. Introduction

As the electrical and electronic industry has been growing rapidly in the recent decades, the labelling of electronic components and final products becomes of increasing importance. For example, serial numbers, bar codes, company logos, production date, are mostly frequently applied for the scanning and control purpose in the production. Compared to the conventional techniques of mechanical engraving, ink printing, and chemical etching, laser marking technique is clean, contactless, and eco-friendly. It is processed with higher velocity and more flexibility. It is applicable on both metal and non-metal materials such as plastics, leathers, and even on non-planar surfaces. Since the marking is in the article itself, it is permanent and abrasion resistant. In fact, laser marking has been widely recognized in a wide range of markets covering communications, IT industry, manufacturing and other applications[1].

Polymer materials behave differently when exposed to laser. For example, laser is transmissible to most polymers when the intensity is low except for PC and PVC. With the increase of the laser intensity, some polymers get carbonization at different degrees and are so-called laser markable such as polyester and styrenic types. PMMA acts differently presenting microbubbles under laser light. However, others are not laser markable, such as polyamides, polyolefin, POM, and thermoplastic elastomers[2]. Therefore, laser marking additives are preferable introduced to render those polymers laser markable, as well as to make the marking controllable. Most of laser marking additives are inorganic compounds, including pearl pigment, photosensitive salt, silicate, metal oxide and carbon black. Occasionally organic additives of halogenated compounds, dye and pigment are combined[3-7]. Figure 1 illustrates different mechanisms of laser marking under different circumstances.
Depending on the color contrast between the marking and the base, the laser marking could be categorized into dark-on-light, light-on-dark, and color-on-color. The marking mechanism is the combination of blackening by carbonization and brightening by microbubbles. Normally plastics materials are marked with yttrium aluminium garnet (Nd: YAG) laser at a wavelength of 1064nm.

Polyamides (PA) are semi-crystallized polymers, which are widely used in electrical and electronic applications. Glass fiber (GF) reinforcement is a common approach to improve overall physical and thermal properties for engineering plastics materials.

In this paper, a light-on-dark type of laser markable glass fiber reinforced polyamide compound was studied. Compounding formulations were optimized to leverage laser marking effect and comprehensive mechanical properties.

2. Experiments

2.1. Raw materials

All the raw materials used in the study were listed in Table 1 as below including supplier and commercial names.

| Description            | Supplier and grade name          |
|------------------------|----------------------------------|
| Polymer                | Invista polyamide (PA)66 U4801   |
| Polymer                | Hunan Yuehua PA 6 YH400          |
| Glass fiber            | CPIC EC301CL                      |
| Lubricant              | Faci Chemicals Zinc stearate     |
| Colorant               | AmeriChem Nigrosine concentrate  |
| Laser marking additive | Merck Iriotec 8835               |

2.2. Compounding formulations

All compounding formulations in the study were based on 30% glass fiber reinforced polyamide 66 (PA66) as shown in Table 2.

| Ref#1 | Ex#1 | Ex#2 | Ex#3 | Ex#4 | Ex#5 |
|-------|------|------|------|------|------|
| PA66  | 69.55| 69.05| 69.12| 69.18| 64.12| 64.18|
| PA6   |      |      |      |      | 5    | 5    |
| GF    | 30   | 30   | 30   | 30   | 30   | 30   |
| Lubricate | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Colorant | 0.25 | 0.25 | 0.18 | 0.12 | 0.18 | 0.12 |
| LM additive | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
2.3. **Extrusion and molding**
Reinforced PA compounds were prepared by twin-screw extruder. Glass fiber was added through side feeder. Other additives were premixed with the base polymer firstly, followed by addition through the main throat.

All testing specimens were prepared by injection molding at temperature range of 260-290°C under medium pressure.

2.4. **Testing**
Mechanical and physical properties were measured according to ISO methods:
- ISO 527 for tensile, including tensile strength, tensile elongation and tensile modulus;
- ISO 178 for flexural, including flexural strength and flexural modulus;
- ISO 180 for notched izod impact;
- ISO 1183 for density;
- ISO 1133 for Melt Flow Rate (MFR).

Laser marking effects were characterized in terms of color difference measured with Panasonic Image Checker PV200, as illustrated in a schematic diagram of Figure 2 as below.

![Figure 2. Color difference evaluation by PV200.](image)

3. **Results and discussions**
All mechanical and physical properties were listed in Table 3 for the reinforced PA compounds under this study.

It was seen the introduction of the laser marking agent has little effect on overall mechanical performance. Both tensile and flexural properties were very much close to or even slightly higher than those of the reference sample, since glass fibers in the formulations contributed mostly to the strength and modulus of the compounds. The impact strength and the specific gravity were not influenced very much due to the similar reasons.

However, an obvious drop was observed in the melt index (roughly 50% drop of Ex#1~3 versus Ref#1), indicating a negative effect of laser marking agent on the flowability. It was well known that flowability plays a critical role in processability and finally in cycle time, thus such a reduction of MFR is unacceptable for molders. In this case, a small amount of PA6 was added in the formulations of Ex#4~5. PA6 possesses much a lower melting temperature compared to PA66 (>40°C), meaning molecules of PA6 are more flexible than those of PA66 at the same temperature range during
processing. Therefore, the flowability was boosted with the introduction of PA6 molecules while the other properties were basically maintained due to the compatibility of PA6 and PA66.

**Table 3. Mechanical and physical properties**

| Item                        | Ref #1 | Ex#1 | Ex#2 | Ex#3 | Ex#4 | Ex#5 |
|-----------------------------|--------|------|------|------|------|------|
| **Mechanical**              |        |      |      |      |      |      |
| Tensile strength (MPa)      | 180    | 182  | 174  | 170  | 168  | 177  |
| Tensile elongation (%)      | 2.5    | 2.3  | 2.8  | 2.4  | 2.5  | 2.4  |
| Tensile modulus (MPa)       | 9980   | 10400| 9850 | 9680 | 9700 | 9500 |
| Flex strength (MPa)         | 200    | 206  | 247  | 249  | 246  | 250  |
| Flex modulus (MPa)          | 8030   | 8119 | 9110 | 8568 | 8229 | 8436 |
| Izod impact (kJ/m²)         | 10     | 7.9  | 11.5 | 8.5  | 7.6  | 8.2  |
| **Physical**                |        |      |      |      |      |      |
| Specific gravity            | 1.4    | 1.4  | 1.4  | 1.4  | 1.4  | 1.4  |
| Melt Flow Rate (g/10min)    | 5.3    | 2.7  | 2.1  | 2.5  | 4.2  | 3.8  |

Evaluations on laser marking are displayed in Table 4 and Figure 3 respectively.

Generally colorant content is a big challenge for laser marking in terms of contrast. When the loading of nigrosine was set at the highest of 0.25%, the broken lines were easily found by visual check (Ex#1). When the loading of nigrosine was decreased, though the grayscales in both laser marking area and base area increased, the increment of grayscales in laser marking area was larger. Consequently, the contrast was improved with the reduction of nigrosine loading (Ex#2 and Ex#4). A further decrease in nigrosine was unnecessary considering the overall aesthetic effect. The optimal formulation was achieved at nigrosine of 0.18% in Ex#4.

The negative influence of nigrosine on contrast might be explained with the microbubble mechanism caused by laser in the system. When the absorption is extremely strong, the polymer base decomposes due to excessive heat. In this case a black pigment type of laser marking additive plays a role of substitution that absorbs the light superbly and prevents the polymer from decomposition. The final effect of laser marking is a combination of blackening by carbonation and brightening by microbubbles [8-9].

**Table 4. Laser marking results**

| Item                        | Ex#1   | Ex#2 | Ex#3 | Ex#4 | Ex#5 |
|-----------------------------|--------|------|------|------|------|
| **Visual check**            | Broken line | ok   | ok   | ok   | ok   |
| **Color difference by PV200**| 3.3    | 5.4  | 5.9  | 6.1  | 5.2  |

**Figure 3.** Final marking of PA66 compounds.

4. **Conclusion**

A laser marking additive was adopted to prepare light-on-dark laser markable glass fiber reinforced polyamide compounds. Both mechanical and physical properties were studied. Nigrosine counteracted laser marking agent because of microbubble mechanism in the system. Laser marking agent decreased the flowability. PA6 benefited flowability to some degree without reduction of mechanical properties.
Optimal formulation was achieved with a combination of medium loading of colorant (0.18%) and a small amount of PA6 loading (5%).

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