

Effect of Additional Laser-Sensitive Pigment on Marking Brightness and Physical Property of Polypropylene Plastic

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Abstract

In this study, laser marking was performed by radiative laser beam having wavelength of 1064 nm onto the surface of polypropylene (PP) specimens with laser-sensitive pigment addition. The different amount of laser-sensitive pigment were added onto the PP plastic in the range from 0 to 4.5 wt%. The effect of laser marking parameters such as laser power, scanning speed and pulse frequency on the contrast between marking pattern and the specimens were investigated. In addition, the physical properties such as tensile strength, elongation at break and heat-resistant of the specimens with laser-sensitive pigment addition were determined. The results showed that the brightness of marking pattern was increased as the amount of pigment was increased due to the high absorption of laser-sensitive pigment in the specimens. The pigment content of 0.6 wt% was achieved for the highest contrast laser marking of PP. For the physical characteristics, PP plastic with laser pigment addition showed the decrease of tensile strength as the laser pigment was increased. However, the laser pigment addition can increase heat-resistance of PP plastic. The optimum laser parameter for maximization of brightness of marking pattern and maintaining the physical property were also found out in this study.

Keywords: laser marking, laser-sensitive pigment, PP plastic, tensile strength

1. Introduction

Indelible marking has been used in various manufacturing such as automotive, electronics, medical and food industries. The manufacturers use direct part marking to identify their components which are able to date codes, product name, bar codes or part numbers and company logos, etc. [1-4]. It is an important role to enable traceability, product unique identification and obstacle product counterfeiting. In general, laser can directly mark on glass, ceramics [3, 5-7], plastics [1-3, 8-15], metals [16-18], stainless steel [4, 19], and organic materials [4, 20] that provide many advantages over traditional methods such as heat pumps, ink-printing, ink-refilling, stamp, handwriting and dot peen marking [1-3, 5]. Because of these methods above mentioned, it is non-permanent marking on a high-density material and a glossy surface, so plastic material cannot absorb ink and hold it in place [2, 3].

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On the other hand, laser marking does not affect the environment and cost-effective management due to it does not use any consumables. It is the most flexible way of marking on plastics that provide a yield legible, high-contrast and indelible, with no direct parts contact with the material other than through the incident laser beam. This method is suitable for using on a complex curved or a rough surface and a small specimen. The automated systems would be designed in accordance with operation and can be moved easily [4, 21]. In addition, it is highly repeatability, high speed marking and reliability. However, the poor conditions of laser speed, laser power and frequency are affected to the low contrast or marks disappear on the material. And the dust control is required in the area where use to operate laser marking machine. If the computer control unit and lens are dirty, it will cause mark distortion. TEA-CO₂ laser, Nd: YAG laser and Excimer laser are currently used for marking on plastic material [1, 3, 22-30]. But, three lasers above mentioned can mark on PP plastic but it doesn't appear of brightly colored. Thus, the pigment and additive systems were considered to enable the contrasting colors and degrees of shading [1, 31]. One of the pigment is (Mica + Fe₃O₄) that uses in additive on PP plastic. In addition, the advantage of this pigment is absorbing laser wavelength and cause the bright color marking [31]. PP plastic is widely used in automotive parts, pipes, tanks, batteries, bottles, packaging, medical equipment, sacks of rice and chemical bottle [32, 33]. It is a thermoplastic polymer that changes properties when heated and cooled. The melting point is approximately 165° to 177° C and a density of 0.90 g/cm³. In addition, it has an excellent chemical resistance property, endurance, shock-resistant structure, lightweight, well formed, medium flexion, does not absorb moisture, high hardness and toughness. However, low temperatures can be more harmful to PP plastic than high temperatures, resulting in brittle and crack. The sun rays do not suitable for PP plastic because it affects to a pale color. Carbon black was also incorporated in a way to improve the property of PP plastic. Antioxidants help prevent thermal oxidation reactions when plastics are exposed to UV light. In this work, we were investigated the effects of (Mica+Fe₃O₄) pigment on the contrast of marking pattern and physical properties of PP plastic such as tensile strength, elongation at break and heat-resistant. The different amount of laser-sensitive pigment was added to the PP plastic in the range from 0 to 4.5 wt% with 0.2 wt% carbon black. The effect of laser marking parameters such as laser power, scanning speed and pulse frequency on the contrast of PP specimens was investigated.

2. Materials and Methods

2.1 Sample preparation

In the study, PP plastic mixing with laser-sensitive pigment (Mica CAS No. 12001-26-2 and Fe₃O₄ CAS No. 1317-61-9, MERCK) were used as laser marking specimens. The amount of laser pigment was varied between 0 and 4.5 wt% and fixed 0.2 wt% carbon black. The specimens were casting by injection molding process for a dimension of 3 in x 3 in x 3 mm (width x length x thickness). Figure 1 shows raw materials containing PP, laser pigment and carbon black. The specimens were laser-marked under the different laser conditions. In order to obtain highly brightness and keeping physical properties such as tensile strength, elongation at break and heat-resistant, the optimum content of laser-sensitive pigment with PP was investigated.

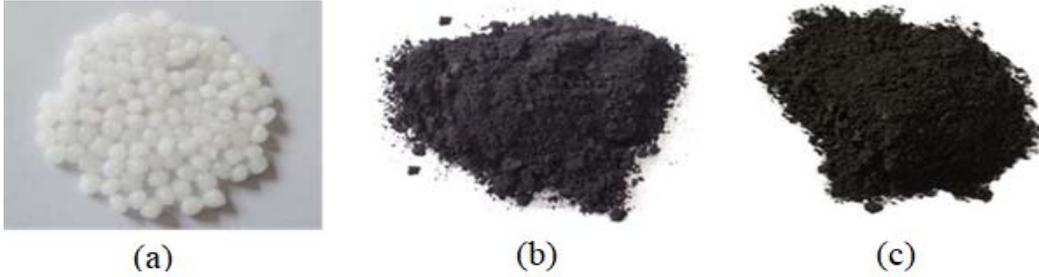


Figure 1. Raw materials (a) PP plastic, (b) laser pigment and (c) carbon black for casting process

2.2 Laser condition setting

In this experiment, Q-switched laser wavelength 1064 nm was used for laser marking. Laser has a maximum power of 20 W and the highest frequency range of 1000 kHz. The characteristics width pulse were 3-500 ns, focal plane diameter less than 20 μ m, pulse frequency up to 75 kHz, pulse energy at 0.7 mJ and the laser focus at 160 mm. Laser condition setting was important for marking brightness, marking depth, and plastic surface melting on the specimens. In this experiment, the variables such as power, frequency and marking speed were setting as shown in Table 1.

Table 1. Laser condition setting (marking speed, laser power, and frequency) for the experiments

Laser Condition Setting			
Experimental	Speed (mm/s)	Power (%)	Frequency (kHz)
1	500 - 2500	100	40
2	1500	75 - 95	40
3	1500	100	20 - 70

2.3 Sample Characterization

2.3.1 Color

The paint software was used to analyze the color of laser marking specimens by using Color Picker mode. Color measurement with paint software was processed through RGB system. In this study, the color that arises from laser marking is white color characteristic. The gray scale image system is available for color level from dark until white colors. The maximum white color level of 255 pixels and dark color level of 0 are defined. The value is the intensity of light/brightness in each of the positions in the gray scale [34-37]. In the order to measure color brightness with the paint software, we developed the setup to take the picture with a digital camera as shown in Figure 2. The lighting conditions were controlled at angle of 90° and it also controlled the condition of the camera to take a picture on the specimens.

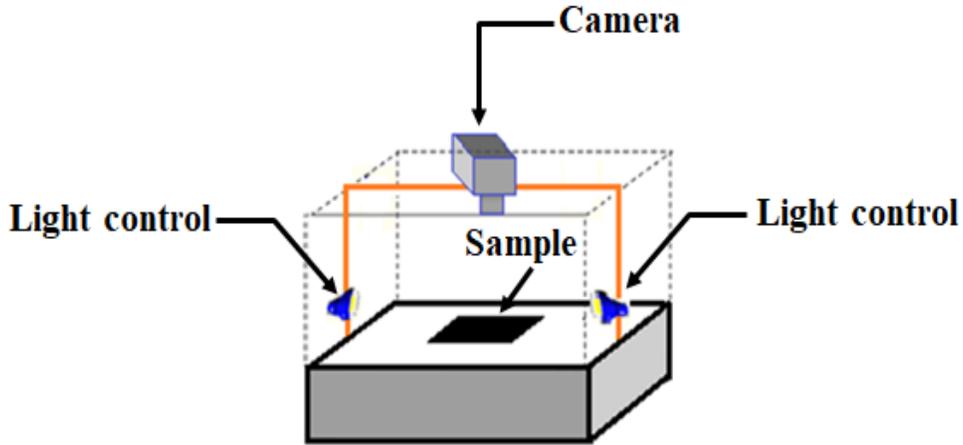


Figure 2. Schematic diagram of camera setup and imaging for laser marking samples

2.3.2 Tensile strength

Tensile strength analysis such tensile strength, Young's modulus and yield strength was used to determine the mechanical properties of laser pigment added in the specimens. The analysis was determined under the ASTM D638 standard. The different content of laser pigment in PP plastic at 0.2 wt%, 1.5 wt%, 3.0 wt% and 4.5 wt% were measured. For sample preparation, we prepared specimens in dimension of 19 mm x 165 mm x 3.2 mm, following the measurement standard [38, 39], as shown in Figure 3(a). After that the specimen brought to fix on both ends in tensile test machine as shown in Figure 3(b). The testing parameters consisted of pulling speed 50 mm/min, room temperature 23 ± 2 °C, and recorded the peak load until the maximum stress. Tensile tests showed the relationship between stress and strain.

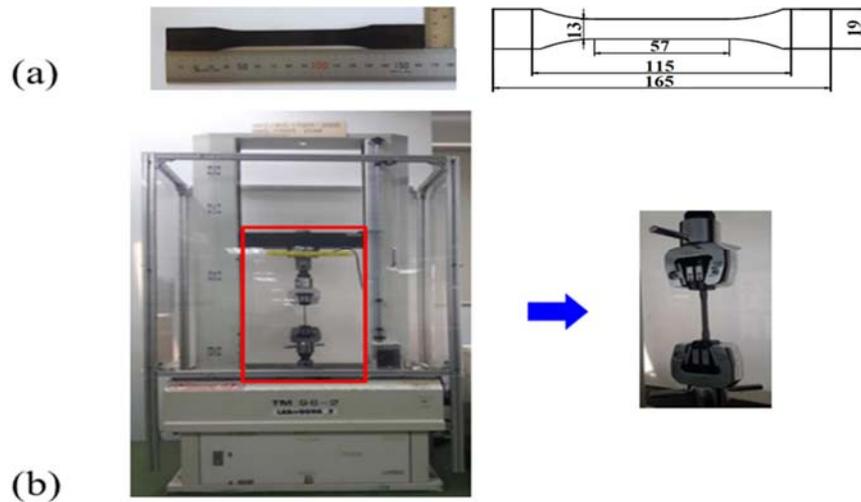


Figure 3. (a) Specimen used for tensile strength testing and (b) Testing equipment

2.3.3 Heat resistance analysis

Thermogravimetric analysis (TGA) is used to analyze the thermal stability of the laser pigment added in the specimens at different contents. Thermogravimetry measures the mass or weight loss of specimens related to temperature or time [40]. The specimens change the weight more or less during the temperature, depending on the characteristic of materials. The lost weight is caused by melting, evaporation or chemical reactions. The test conditions were shown as following; temperature at test start 50°C, maximum test temperature 600°C, temperature rising at 10°C/min.

3. Results and Discussion

3.1 Effect of laser pigment content on color brightness

The marking pattern was defined by the shape to the square 1cm x 1cm on PP plastic specimens with dimension of 3 in x 3 in x 3 mm as shown in Figure 4.

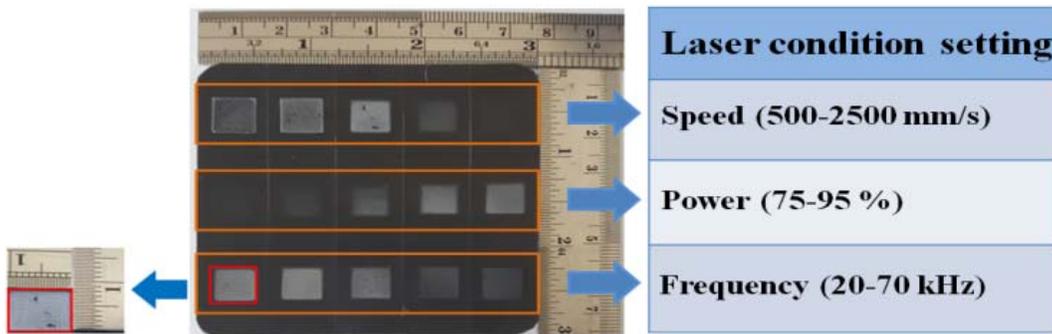


Figure 4. PP plastic specimen with dimension of 3 in x 3 in x 3 mm and color brightness analysis area of 1 cm x 1 cm by different laser condition setting

Figure 5 shows the color brightness of marking pattern with different laser-sensitive pigment content. It was obtained by paint software as shown in Table 2. The results presented in red, green and blue (RGB), following by $Y = 0.3R + 0.59G + 0.11B$ [36, 37]. It was found that the color brightness of the specimen without laser pigment was 56. The color brightness was obviously increased to 168 as the laser-sensitive pigment was increased up to 0.6 wt%. However, the laser-sensitive pigment beyond 1.0 wt% became the lower brightness levels. The color brightness was decreased from 168 to 46 as increase the laser-sensitive pigment to 4.5 wt%. It may be caused by the opaque of laser-sensitive pigment that affected the heat-chemical reaction. The laser-sensitive pigment permeated into the PP plastic and could not melt at the processing conditions. A high opaque was found at the excess laser-sensitive pigment or the poor condition that induced a low laser absorption and lower color brightness [1]. Laser-sensitive pigment of 0.6 wt% was optimized because the laser interaction with the material was complete. Indirect parameters such as, the surface texture of the specimen, the particle size distribution of pigments and the image brightness for shooting are an important role to control the quality of marking.

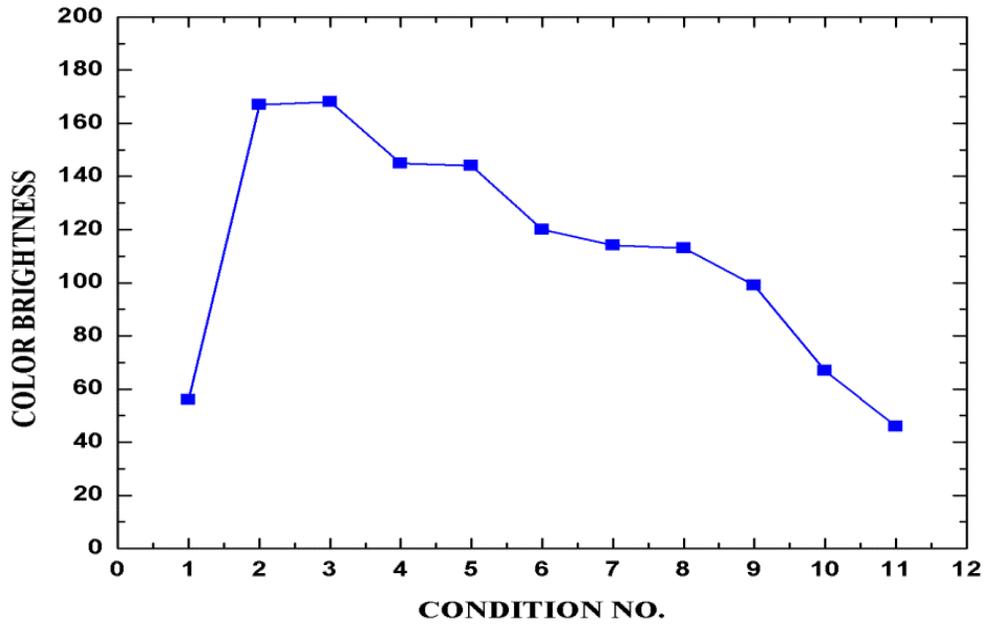


Figure 5. Color brightness of marking pattern on different amount of laser-sensitive pigment specimens

Table 2. Color brightness of marking pattern on different amount of laser-sensitive pigment specimens

Condition No.	Laser-Sensitive Pigment Content (wt%)	Color Brightness (Y)
1	0.0	56
2	0.2	167
3	0.6	168
4	1.0	145
5	1.5	144
6	2.0	120
7	2.5	114
8	3.0	113
9	3.5	99
10	4.0	67
11	4.5	46

3.2 Effect of laser condition setting on marking brightness

From the analysis results, 0.6 wt% of laser pigment was suitable for laser marking on PP plastic. Therefore, this content was chosen to study the laser marking parameters such as laser speed, power and frequency. Figure 6 shows the measurement results of color brightness in different setting speed at 500 mm/s, 1,000 mm/s, 1,500 mm/s, 2,000 mm/s and 2,500 mm/s with power at 100% and frequency at 40 kHz. The results shown that the speed at 1,500 mm/s provided the maximum marking brightness. For the speed setting lower than 1,500 mm/s, the color brightness was decreased due to melting of specimen surface. The surface of the specimen absorbed longer period of the laser energy, heated up, and melted. For the speed setting more than 1500 mm/s, the brightness of the marking pattern was gradually reduced as shown in Figure 6. It was due to the incomplete of decomposition reaction of laser pigment and laser energy. This result indicated that the laser scan speed was another important parameter for laser marking.

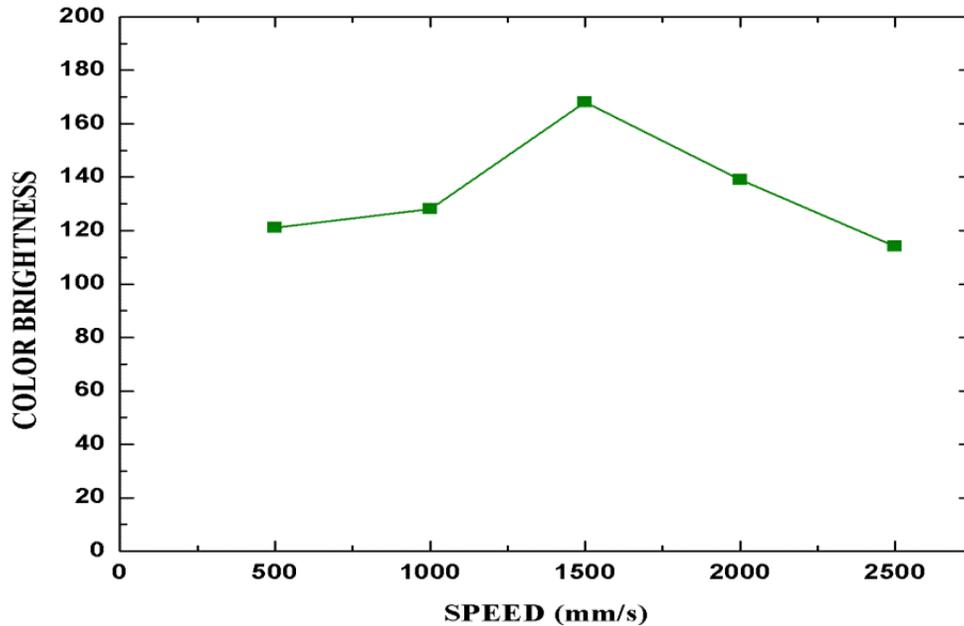


Figure 6. Color brightness of marking pattern as a function of laser speed on laser-sensitive pigment of 0.6 wt% specimen

Figure 7 shows the results of color brightness with the different laser power setting at 75%, 80%, 85%, 90% and 95%. The speed and frequency of laser was fixed at 1500 mm/s and 40 kHz, respectively. The maximum color brightness was obtained at the power of 95%. It was due to the high energy induced- melting of laser pigment that affect to the color reaction [3]. In addition, the suitable of laser speed and frequency were significant to the marking brightness.

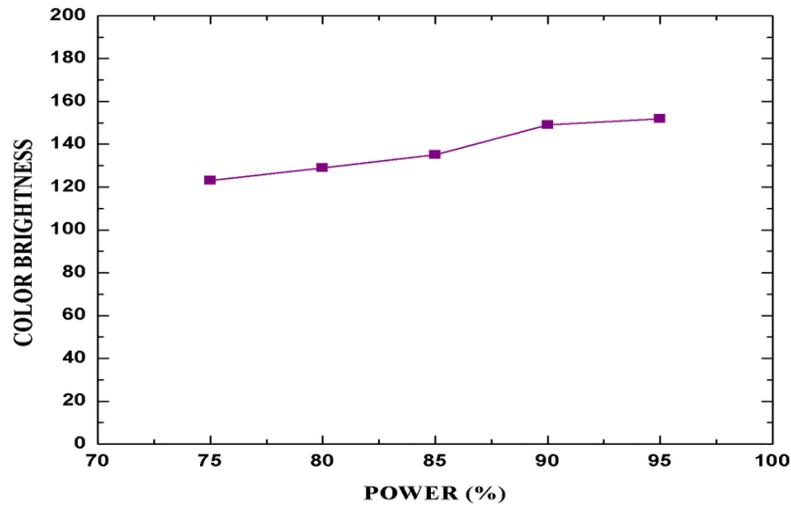


Figure 7. Color brightness of marking pattern as a function of laser power on laser-sensitive pigment of 0.6 wt% specimen

The difference of laser frequency was studied at 20 kHz, 35 kHz, 50 kHz, 65 kHz and 70 kHz under maintaining scan speed and power of 1,500 mm/s and 100%, respectively. Figure 8 shows the color brightness of the marking pattern on the specimen with 0.6 wt% pigment as a function of laser frequency. The color brightness was similar for the laser frequency of 20 to 35 kHz. However, the color brightness decreased as the increase of laser frequency from 35 to 70 kHz. It causes by the excessive repeatability per one pulse that affected to overlapping densities of the marking lines [4].

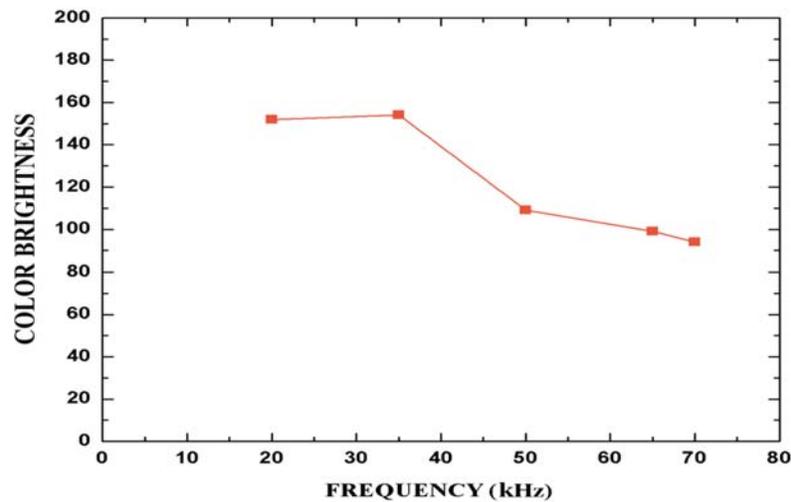


Figure 8. Color brightness of marking pattern as a function of laser frequency on laser-sensitive pigment of 0.6 wt% specimen

3.3 Effect of laser-sensitive pigment on physical property

Load versus elongation curve of specimens with different amount of laser pigment is shown in Figure 9. The calculation parameters such as tensile strength, Young’s modulus, and yield strength were obtained in Table 3. The results shows that tensile strength, Young’s modulus, and yield strength were slightly decreased as the laser pigment was increased from 0.2 wt% to 4.5 wt%. This result indicated that a small addition of laser pigment slightly affected the physical property of PP plastic. It caused by the laser pigment permeates into the PP plastic as foreign matter that affect physical properties on PP plastic.

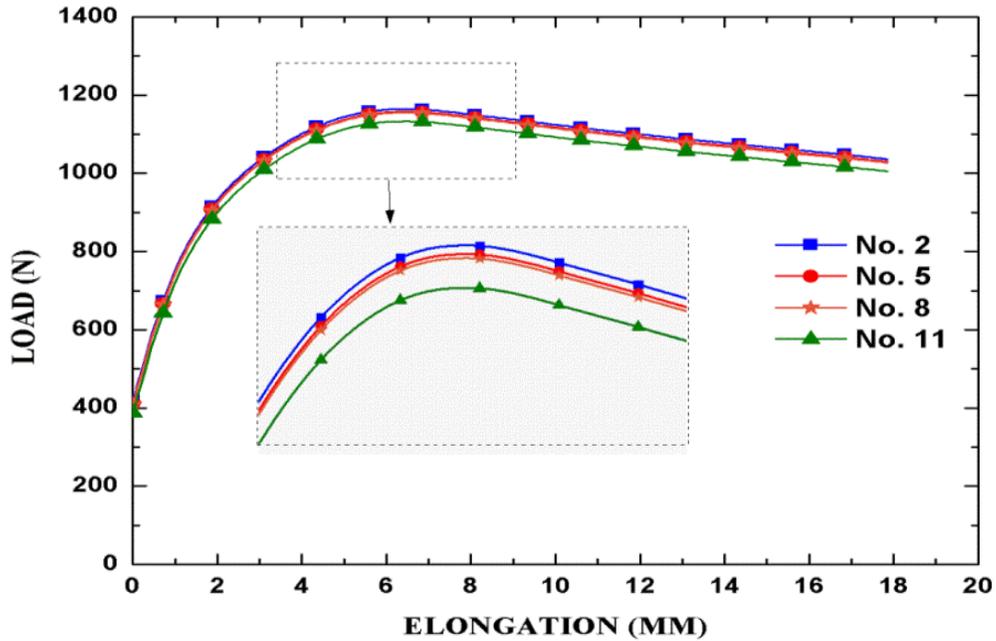


Figure 9. Tensile strength of PP plastic with the different amount of laser-sensitive pigment

Table 3. Tensile results of PP plastic with the different amount of laser-sensitive pigment

Condition No.	Test Results76				
	Laser-Sensitive Pigment (wt%)	Tensile Strength (N)	Tensile stress (MPa)	Young Modulus (MPa)	Yield Strength (MPa)
2	0.2	1164.614	27.996	426.520	21.870
5	1.5	1158.113	27.840	423.413	21.576
8	3.0	1155.169	27.766	415.406	21.296
11	4.5	1133.544	27.250	405.853	20.810

3.4 Effect of laser pigment on heat resistance

The heat resistance of the specimens was analyzed by thermogravimetric (TGA) in the thermogram pattern as shown in Figure10. The value of decomposition temperature was determined by a point that the specimen was lost the weight. The heat resistance was directly proportional to the decomposition temperature. It was found that the decomposition temperature of specimens depended on the content of laser pigment addition. The decomposition temperature increased from 314.38°C to 338.35°C as the laser pigment was increased from 0.2 wt% to 1.5 wt%. However, the temperature decreased after the laser pigment was increased from 1.5 wt% to 4.5 wt%, as shown in Table 4. The excessive laser pigment was not beneficial because it became a foreign matter on PP plastic. Thus, 1.5 wt% of laser pigment addition was suitable to enhance the heat resistance of PP plastic.

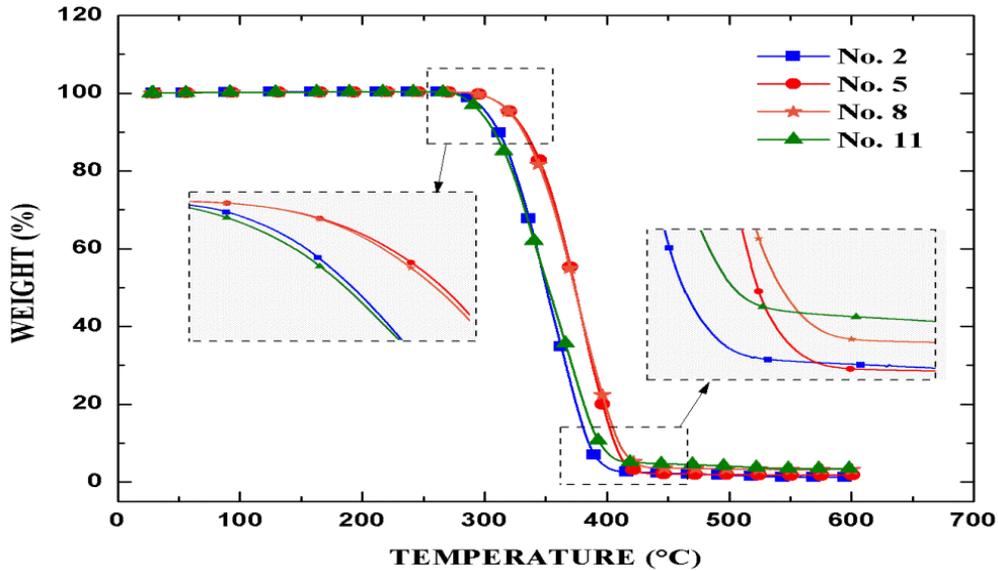


Figure 10. Heat resistance by Thermogravimetric Analysis (TGA)

Table 4. TGA measurement of specimens with different amount of laser-sensitive pigment

Condition No.	Laser-Sensitive Pigment Content (wt%)	Test Result	
		Temp (°C)	Weight (%)
2	0.2	314.38	98.865
5	1.5	338.35	98.298
8	3.0	335.35	96.826
11	4.5	305.14	96.609

4. Conclusions

The effect of laser-sensitive pigment addition on color brightness and physical property of PP plastic was investigated by using Q-switches laser making. The color brightness and physical property corresponded with the laser pigment content. The optimum laser pigment of 0.6 wt% was obtained that achieves both maximum color brightness and maintaining the physical property of PP plastic. In addition, laser parameters consisting of power, and speed were important factors to control the color brightness. Laser setting of speed at 1,500 mm/s, power at 100% and frequency at 40 kHz were optimized for the maximum color brightness on the laser-sensitive pigment of 0.6 wt% specimen. In the addition, the results of the physical properties of PP plastics revealed that small amount of laser-sensitive pigment slightly affect to tensile strength, Young's modulus, yield strength while it helped to increase heat-resistant of the specimens. Therefore, the appropriate laser pigment must be taken into consideration.

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