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Influences of diantimony trioxide on laser-marking properties of thermoplastic polyurethane

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The influences of diantimony trioxide (Sb_2O_3) on the laser-marking properties of thermoplastic polyurethane (TPU) are studied. The TPU/Sb_2O_3 composites are prepared by melt blending in a HAAKE mixer. A neodymium-doped yttrium aluminum garnet (Nd:YAG) pulsed laser beam of a wavelength of 1064 nm is used to scan the surfaces of the composites to create markings. Visual and microscopic analyses of the TPU/Sb_2O_3 composites after laser treatment show high-contrast black markings, depending on the Sb_2O_3 loading, Sb_2O_3 particle size, and laser-beam power. The laser-marking properties of the composite surfaces are analyzed by X-ray diffraction, Raman spectroscopy, and thermogravimetric analysis. Furthermore, a mechanism for the laser-induced darkening of the TPU/Sb_2O_3 composites is proposed. The Sb_2O_3 particles absorb laser energy and convert it into thermal energy. This causes the surrounding TPU matrix to carbonize into amorphous carbon, forming black markings.

1. Introduction

Recently, the demand for surface-decorated plastic products has increased. Consequently, product-specific patterns and information are displayed on the surface of plastic products. However, traditional techniques such as painting [1], ink marking [2], and screen printing [3] are cumbersome and are accompanied by serious environmental problems. Chemical additives and reactions used in these traditional techniques lead to the formation of many toxic and hazardous substances on the plastic surface, limiting the application of the product. Fortunately, this problem can be avoided by using laser-marking technology; this technology is more eco-friendly than the traditional techniques and has advantages such as high precision and persistence, short manufacturing cycles, flexibility, and contactless handling [4–6]. The principle of laser marking is that laser energy is absorbed by the polymer matrix and converted into thermal energy. When the thermal energy reaches a certain value, it triggers various physical and chemical changes within the polymer matrix, resulting in marking effects [7]. For example, polymers such as polyethylene terephthalate [8], polybutylene terephthalate [9], polycarbonate [10], and polystyrene [11] can be easily carbonized under laser irradiation and are suitable for dark markings. In addition, polymers such as polyformaldehyde [12] and poly (methyl methacrylate) [13] can be easily foamed under laser irradiation and are suitable for light markings.

However, some common polymers such as polyethylene, polypropylene, and thermoplastic polyurethane (TPU) are inefficient for absorbing a laser beam of a wavelength of 1064 nm [14–16]. No obvious physical and chemical changes are observed on the surface of the material after laser irradiation. Furthermore, increasing the laser-beam power and laser exposure time significantly improves the quality of laser marking and increases the cost. A simple and effective method to improve the laser-marking properties of polymers is to incorporate laser-sensitive additives in the polymers. Laser-sensitive additives such as mica [17], bismuth oxide (Bi_2O_3) [18], bismuth oxychloride (BiOCl) [14], stannic oxide (SnO_2) [19], and titanium dioxide (TiO_2) [20] can efficiently absorb laser energy and carbonize the surrounding polymer matrix to generate high-

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definition, high-contrast, and damage-free surface markings. Zhong et al. [18] prepared TPU/Bi_2O_3 composites with excellent laser-marking performance. The local carbonization through TPU thermal degradation and the reduction of Bi_2O_3 to black bismuth metal synergistically contributes to the formation of black markings on the composite surfaces. However, the addition of yellow Bi_2O_3 particles makes the TPU matrix appear yellow, which restricts the application of the TPU/Bi_2O_3 composites in the field of white materials. On this basis, Cao et al. [14] used BiOCl as the laser-sensitive additive and TPU as the polymer matrix to prepare TPU/BiOCl composites with a white background. Zheng et al. [20] used TiO_2 to enhance the laser-marking contrast of thermoplastic elastomers. Moreover, the marking contrast and material translucency can be controlled by varying the TiO_2 content. As more and more polymer products are developed, more advanced laser-marking methods for these products are required.

TPU, an important thermoplastic elastomer that is wear-resistant, oil-resistant, transparent, and flexible, has been broadly utilized in daily necessities, sporting goods, toys, decorative materials, and other applications [21–23]. Laser marking on the surface of TPU products can provide indispensable information, such as production date, place of origin, company logo, and quick response code. Antimony trioxide (Sb_2O_3), a white crystalline powder, has been widely used in fireproof white pigments and paints [24–26]. In the present study, white Sb_2O_3 particles of three sizes were selected to improve the laser-marking properties of the TPU matrix. TPU/Sb_2O_3 composites were prepared by simple melt blending in a HAAKE mixer. Then, a beam-controlled Nd:YAG laser beam with a wavelength of 1064 nm was used to create markings on the surfaces of the composites in air atmosphere. The sharpness and contrast of the laser markings on the surfaces of the TPU/Sb_2O_3 composites were investigated under different marking conditions. The marked surfaces were characterized using various microscopic techniques, Raman spectroscopy, X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Furthermore, a mechanism for laser-induced darkening of the TPU/Sb_2O_3 composite surfaces was proposed.

2. Experimental section

2.1. Materials

TPU (aromatic TPU, EX-85 A) was purchased from Gaoding Chemical Company, Taiwan. Analytical grade antimony trioxide (Sb_2O_3) with particles of three sizes (0.1, 0.3, and 0.6 μm) was purchased from Sinopharm Chemical Reagent Company, China.

2.2. Sample preparation

A series of TPU/Sb_2O_3 composites were prepared using a HAAKE mixer (HAAKE Rheocord 9000) at a rotational speed of 50 rpm and 190 °C for 10 min. The particle sizes of the Sb_2O_3 added to TPU were 0.1, 0.3, and 0.6 μm. The Sb_2O_3 contents added to TPU were 4, 6, and 8 wt%. The obtained samples were labeled as "TPU/Sb_2O_3-Sb_2O_3 size-Sb_2O_3 content" (e.g., "T/S-0.1-4" refers to the TPU/Sb_2O_3 composite containing 4 wt% of 0.1 μm Sb_2O_3). Each composite sample was pressed into a sheet with a thickness of 2 mm using a compressing machine (10 MPa, 190 °C).

2.3. Characterization

A beam-controlled Nd:YAG laser-marking system (KDD-50, Suzhou KiTe Laser Technology, China) with a wavelength of 1064 nm was used to create markings on the surfaces of the sheet samples. The focal length and spot size of the laser beam were 219 mm and 100 μm, respectively. The laser sweep speed was set to 450 mm/s, and the pulse repetition frequency was 3.9 kHz. The laser-beam powers were set to 18.5, 21.0, 23.5, 26.0, and 28.5 W.

A digital camera (DSC-RX100, Sony Co.) was used to observe the overall effect of the laser-induced markings. A metalloscope (ECLIPSE-LV150 N, Nikon Co.) and stereomicroscope (XTD-211, Phoenix Technology Co.) were used to observe the morphology of the surfaces and sections of the samples before and after laser marking. Scanning electron microscopy (SEM; QUANTA250FEG, FEI Co., Czech Republic) was used to observe the morphology of the fractured surfaces of the sheet samples. The mean size of Sb_2O_3 was determined by randomly measuring the size of 50 different particles in the SEM images using a dimensional analysis software (Nano Measure V.1.2.5). The chromatic aberration between the markings was measured using a colorimeter (CM-5, KONICA MINOLTA, China).

The XRD patterns were measured on a powder diffractometer (RINT2000, Rigaku) using Cu Kα radiation at a wavelength of 1.54 Å. The samples were scanned in a 2θ range of 5°–70° at a scanning rate of $0.02° \cdot S^{-1}$.

The surfaces of the TPU/Sb_2O_3 composites before and after laser marking were characterized by a DXR laser Raman spectrometer (Thermo Science and Technology Co.) with a laser wavelength of 780 nm, laser power of 7 mW, and slit width of 50 μm.

The thermal properties of the TPU/Sb_2O_3 composites were measured on a thermogravimetric analyzer (NETZSCH-TG 209 F1, NETZSCH Co., Germany). The heating rate was 10 $°C \cdot min^{-1}$, and the gas environment was nitrogen.

3. Results and discussion

3.1. Laser-marking properties of TPU matrix

Fig. 1(a) and (b) shows the stereomicroscopic images of the TPU matrix before and after laser marking. It can be seen that there are almost no obvious changes on the surface of the TPU matrix after laser marking, and only a few obscure black spots can be observed at high magnification. Therefore, the TPU matrix has almost no laser-marking properties. To further understand the changes in the TPU matrix before and after laser marking, TGA curves are shown in Fig. 1(c). Under oxygen atmosphere, the TGA curves of the TPU matrix before and after laser marking basically overlap. Due to the special structure and transparency of the TPU matrix, it cannot easily absorb laser energy and undergo a chemical or physical reaction (e.g., foaming, carbonization, and discoloration) [18]. Thus, laser marking using a Nd:YAG laser beam of 1064 nm has almost no effect on the surface of the TPU matrix.

3.2. Morphology and structure of Sb_2O_3 particles

SEM images as well as the size distribution of three types of Sb_2O_3 particles are shown **in** Fig. 2(a), (b), and (c). In Fig. 2(a), the nominal size is about 0.1 μm. As can be observed, agglomeration is most obvious in these particles due to their small size. In Fig. 2(b), the nominal size is about 0.3 μm. Some Sb_2O_3 particles with complete orthorhombic crystal structures can be observed. In Fig. 2(c), the nominal size is about 0.6 μm. The orthorhombic crystal structures of the Sb_2O_3 particles are more complete, but their size distribution is wide. In addition, the XRD patterns of the three types of Sb_2O_3 particles are shown in Fig. 2(d). All three types have the same crystal structure, and only show different particle size distributions.

3.3. Effect of particle size of Sb_2O_3 on laser-marking properties

The visual effects of the "TPU" characters and the open and solid