Recognition of laser-marked quick response codes on polypropylene surfaces

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ABSTRACT

Polystyrene-grafted antimony trioxide (Sb_2O_3-g-PS) was prepared as a laser-marking additive by free radical polymerization. Fourier transform infrared spectroscopy, scanning electron microscopy, and transmission electron microscopy were used to characterize the modified Sb_2O_3 particles with a core-shell structure. Composites of polypropylene (PP) and modified or unmodified Sb_2O_3 were laser-marked using a neodymium-doped yttrium aluminum garnet laser at 1064 nm. Compared with PP and unmodified Sb_2O_3 composites, the laser marking performance was dramatically improved for PP composites, with an equivalent amount of Sb_2O_3-g-PS. The marking patterns of quick response (QR) codes on the surface of PP composites containing Sb_2O_3-g-PS were clear and had a high contrast. The QR codes were easily and quickly recognized when the content of Sb_2O_3-g-PS reached 2.0 wt%. The laser-induced blackening on the surface of the PP/Sb_2O_3-g-PS composite was due to the synergistic effect of Sb_2O_3 photothermal conversion and PS carbonization, which can effectively improve the laser marking performance and QR code recognition. We believe that the application of this core-shell laser additive will become prominent in the field of QR code marking, for polyolefins that are poor absorbers of the 1064 nm wavelength.

1. Introduction

It has been recently reported that material surfaces can be easily laser marked due to color alterations induced by chemical/physical changes during laser irradiation, such as carbonization, foaming, and melting [1–3]. Compared with traditional methods involving the use of inks and toxic solvents, laser marking has a high precision with low environmental pollution [4,5]. In addition, the impact of laser marking with high reliability is more pronounced in the fields of plastics, metals, ceramics, clothing, and food packaging that helps meet the high demands of fineness and smoothness [6]. Neodymium-doped yttrium aluminum garnet (Nd:YAG) lasers with a wavelength of 1064 nm are the most ideal for laser marking metals and plastics. It is also one of the most widely used lasers in medicine and laser processing [7–9].

Polymers such as poly(ethylene terephthalate) (PET), polycarbonate (PC), and polystyrene (PS) are laser sensitive to the 1064 nm wavelength. They can be directly laser marked due to their high char residue and facile carbonization at high temperatures. The residual carbon content of polymers with a high char yield such as PC, polyphenylene oxide (PPO), and polyimide (PI) can reach up to 20–50 wt% at 800 °C [10–12]. However, high-density polyethylene (HDPE) and polypropylene (PP) are poor absorbers of the 1064 nm wavelength and hardly undergo color changes. PP is a semi-crystalline thermoplastic and is widely used in the automotive, machinery, and piping industries due to its lightweight, solvent resistance, and processability [13,14]. When used for automotive interior trims or packaging, it is usually necessary to mark texts, graphics, and QR codes [15]. The demand for QR code laser traceability is increasing for the automotive and packaging market. Currently, marking of QR codes is the focus of laser marking research [16]. Therefore, it is desirable to enable laser marking of QR codes on PP surfaces as proposed in this study. However, PP itself cannot be carbonized as it does not absorb the 1064 nm wavelength. Hence, the addition of laser-sensitive additives or laser absorbents to PP can improve the laser marking performance [17].

A large number of studies have investigated the influence of laser-sensitive additives on the laser marking properties of polymers. Zheng

et al. [18] developed a method for achieving high contrast marks on thermoplastic elastomers by adding TiO_2 particles. The marking quality and material translucency were determined by varying the TiO_2 content. Liu's group [19–21] have studied the laser-induced blackening of thermoplastic polyurethanes mixed with inorganic pigments containing bismuth. It was found that the marking contrast on the composite surfaces, after laser irradiation, was due to the synergistic effects of carbonization via polymer pyrolysis and the decomposition of bismuth oxide. The laser marking of polymers is achieved by burning the polymer chains surrounding the laser-sensitive inorganic particles. Hence, the ability of the polymer matrix to form carbonized materials is critical for the marking effect. The residual carbon content of PP is almost zero at high temperatures and is recognized as one of the most difficult polymers to laser mark. Various types of polymer/inorganic composites and laser-marking mechanisms have been investigated. However, the development of a suitable laser-marking additive for producing high-contrast and durable laser marks on PP is still required.

Antimony trioxide (Sb_2O_3) is a photocatalyst that is widely used for laser marking plastics [22,23]. A company called DSM (Netherlands) have developed Sb_2O_3 laser marking additives that can significantly increase the marking contrast of nylon 6 [24]. Although, the direct incorporation of inorganic additives in polymers is a simple and facile method, the inorganic additive is unable to improve the marking performance of PP. Zhang et al. [25] reported nano-antimony-doped tin oxide (nano-ATO) physically coated with a layer of PC with high char residue, via a simple high-speed-mixer solvent-evaporation technique. When the modified nano ATO particles were mixed with HDPE at high temperatures, the marking contrast of HDPE improved. Chains of PC can be adsorbed onto the ATO particles to prepare core-shell structures. However, the PC-coated ATO particles are unstable and the PC chains can be removed by high shear stress during the melt extrusion process. Compared to the physically adsorbed coating, a polymerization method would be more suitable for attaching polymer chains onto inorganic particles to form stable core-shell structures. It has been reported that PS can be easily grafted onto inorganic particles [26,27]. In addition, after laser marking at 1064 nm, PS can absorb energy from the Sb_2O_3 particles, which, however, is sufficient for carbonization, resulting in a higher marking contrast. Hence, PS is the most ideal candidate for improving the laser marking performance of PP. In our work, PS-grafted Sb_2O_3 (Sb_2O_3-g-PS) laser-marking additives were prepared by free radical polymerization to form core-shell structures. Laser marking patterns of PP/Sb_2O_3-g-PS composites were fabricated by a Nd:YAG laser at 1064 nm. Their subsequent applicability to industrial two-dimensional QR codes was also investigated. Raman spectroscopy, visible observations, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and ultraviolet-visible-near infrared spectroscopy were employed to reveal the laser-induced blackening on the composite surfaces.

2. Material and methods

2.1. Materials

Analytical grade Sb_2O_3 was purchased from Hunan Yiyang material factory (Hunan, China). The silane coupling agent 3-(trimethoxysilyl) propyl methacrylate (KH570, 97%) was supplied by Shanghai Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China). Styrene (St, 99%) was purchased from Jiangsu Yonghua Chemical Technology Co., Ltd (Jiangsu, China). Polyvinylpyrrolidone (PVP, K-30, Mw = 40 000, 99.0%) was supplied by Shanghai Qiangshun Chemical Reagent Co., Ltd (Shanghai, China). Analytical grade 2,2′-azobisisobutyronitrile (AIBN, 99.0%) was purchased from Zhengzhou Shengkai Co., Ltd (Zhengzhou, China) and recrystallized from ethanol. Tetrahydrofuran (THF, 99.0%) was purchased from Jiangsu Qiangsheng Chemical Co., Ltd (Jiangsu, China). Polypropylene (PP, B393G), with a melt index of 20 g in 10 min (190 °C/2.16 kg), was obtained from Korean SK Co., Ltd (Seoul, Korea).

2.2. Modification of Sb_2O_3 with silane coupling agent

Sb_2O_3 (2.0 g) particles were dispersed in 120 mL of ethanol, ultrasonically dispersed for 30 min, and then mechanically stirred at 500 RPM at room temperature. Next, 5 mL of KH570 was dissolved in 20 mL of anhydrous ethanol, followed by the addition of deionized water (2 mL) for hydrolysis. The prepared KH570 solution was slowly added to the Sb_2O_3 suspension in ethanol, and refluxed at 80 °C for 6 h. The mixture was centrifuged for 5 min at 6000 RPM. The supernatant was discarded and the precipitants were washed twice with ethanol and subsequently dried under vacuum at 50 °C for 24 h. The chemically attachment of more than one KH570 molecule on the surface of Sb_2O_3 particles leads to the function of the modified Sb_2O_3 particles as cross-linker.

2.3. Synthesis of PS-grafted Sb_2O_3 particles

The Sb_2O_3 particles modified by KH570 (1.5 g) and 2.0 g of PVP were dissolved in ethanol and ultrasonically dispersed for 30 min. The mixture was then transferred into a 250 mL three-necked round-bottom flask fitted with a condenser and a thermometer, and 10 mL of styrene monomer containing 0.1 g of initiator (AIBN) was slowly added drop-wise. The polymerization reaction was carried out under nitrogen for 20 h. In addition, the cross-linking took place when more than one KH570 monomer anchored on Sb_2O_3 surface were polymerized into the same polymer chain. To purify the Sb_2O_3 particles coated with the cross-linked PS layer, excess PVP was washed several times with absolute ethanol and THF. After subsequent drying and grinding, white powders of Sb_2O_3-g-PS particles were obtained.

2.4. Preparation of polypropylene composites

The PP composites were prepared by mixing different quantities of Sb_2O_3 particles before and after modification with the cross-linked PS layers, by mechanical melt blending in a torque rheometer for 3 min at 190 °C. The different compositions consisted of 0, 0.5, 1.0, 2.0, and 3.0 wt% Sb_2O_3 particles (by weight of PP). Sheets of PP with a thickness of ~2 mm were fabricated using a flat vulcanizing machine (XLB-D350, Rubber Equipment Co., Ltd, Changzhou, China) operating at 190 °C. The PP composite samples are labeled with the code "PP/percentageSb_2O_3", i.e., "PP/2.0%Sb_2O_3" refers to PP composite with 2.0 wt% Sb_2O_3.

2.5. Laser marking PP composites

Laser marking of the composite sheets was performed on a beam-controlled Nd:YAG laser (KDD-50, Suzhou KiTe Laser Technology, China) at a wavelength of 1064 nm. The laser beam was reflected and deflected by a polarized mirror, and then projected onto the surface using a lens that produced a dot size of 0.2 mm in diameter. The laser sweep speed was set to 450 mm s^{-1}, while the pulse repetition frequency was 4.0 KHz. Software (EzCad2.7.0, Suzhou KiTe Laser Technology, China) permitted the design and generation of various marking symbols and tuning of laser parameters including laser power. The QR code was laser processed onto a square area of 4 cm^2, encoding the Changzhou University Website (http://www.cczu.edu.cn). A smart phone with the free QR code reader application was used to evaluate the readability of the QR codes marked on the samples, treated at various laser powers ranging from 20.9 to 24.8 W.

2.6. Chemical and physical characterization

The Raman spectra for Sb_2O_3 before and after modification, and PP composite surfaces were obtained on a DXR laser micro-Raman