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Study of Laser-Marking Properties and Mechanism of PBT/SnO₂

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Abstract: High quality laser markings can be easily produced on surfaces of poly(butylene terephthalate) (PBT) by simple dispersing stannic oxide (SnO₂) in PBT melt, and followed by a laser irradiation procedure in order to improve the laser marking performance of PBT. Compared with the pure PBT sample, the PBT/SnO₂ samples after the beam-controlled laser irradiation showed higher marking contrast and edge acuity, depending on the SnO₂ loading content and laser power in terms of the visual observations and microscope analysis. In addition, the marking quality and readability of the laser markings for the industrial use as the two-dimensional quick response (QR) codes were tested for the PBT/SnO₂ material under various laser power condition. The laser irradiated material surfaces were characterized by using SEM, XRD, Raman spectroscopy, TGA and DSC. The results indicated that the formation of the black-colored marks on sample surfaces was due to the laser absorption at the irradiation wavelength of 1 064 nm by the SnO₂ particles and localized heating of the surrounding PBT chains, leading to the generation of the amorphous black carbonized materials without changing the crystal structures of SnO₂.

Key words: laser marking; poly(butylene terephthalate); stannic oxide; contrast; carbonization

PBT/SnO₂ 的激光标记性能及机理研究

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摘要:为改善聚对苯二甲酸丁二醇酯(PBT)的激光标记效果,通过将二氧化锡(SnO₂)分散在PBT熔体中制备PBT/SnO₂材料,经激光辐照处理,在材料表面产生清晰的激光标记图案。通过肉眼观察和显微分析发现,与纯PBT相比,PBT/SnO₂材料在激光辐照后具有较高的标记对比度和边缘锐度,取决于SnO₂加入量和激光功率参数。此外,在不同激光功率条件下考察了PBT/SnO₂材料表面产生的二维码(QR)的标记质量和机器可读性。使用扫描电镜(SEM)、X射线衍射(XRD)、拉曼光谱、热重分析(TGA)和示差扫描量热仪(DSC)对激光标记表面进行表征分析。结果表明PBT/SnO₂材料表面激光标记的形成是由于SnO₂颗粒吸收1 064 nm波长激光的辐射能量,使颗粒周围PBT分子链局部受热发生热解炭化,从而导致无定型黑色碳类物质的生成,过程中没有发生SnO₂晶型结构的变化。

关键词:激光标记;聚对苯二甲酸丁二醇酯;二氧化锡;对比度;炭化

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In modern industry, various markings such as numbers, characters, and symbols on products are mostly made using conventional techniques, such as ink marking and screen printing. Laser marking as an attractive technique for the recognition, identification, and decoration of products made from the polymers, ceramics and metals, providing valuable information including production dates, expiration dates, company logos and serial numbers on these material surfaces, is gaining widespread interest^[1-3]. The exposure of various materials to the laser beam can induce physical and/or chemical changes, leading to permanent and high contrast marks, micropatterns^[4], and nanostructures^[5] on the material surface without using expensive consumable ink/solvents or post-curing^[6]. In recent years, laser marking has been well established industrial laser application duo to its short fabrication cycle, high processing precision, flexibility, contact-free treatment, and ecological friendliness^[7]. In addition, laser induced markings are durable, since they are within materials and have a penetration depth ranging from micrometer to millimeter order. In fact, as the use of laser marking technique becomes more widespread in numerous industries including food package, automotive industry, appliances, and electronics, for marking specific plastic parts and components, there is a growing need to obtain a deep understanding of laser interaction with different materials and to develop the laser marking materials^[8].

Concerning laser marking in polymers, poly(ethyleneterephthalate) (PET), polycarbonate (PC), and polystyrene (PSt) can produce the black-colored marks after laser irradiation due to their high char residue and feature of easy carbonization at the high temperature^[9]. However, these marks made on surfaces are usually of low quality and do not seem to be suitable and promising for the deep black, high contrast, and two-dimensional machine-readable markings such as

data matrix and quick response (QR) codes. Other polymer materials such as high density polyethylene (HDPE) and polypropylene (PP) without adding laser sensitive pigments are not intrinsically sensitive to the laser beam or undergo hardly chemical and physical changes after laser irradiation^[10].

To improve greatly the capability of these polymers for laser marking, the polymer can be modified with the laser sensitive components including dyes^[11] and pigments by physical and chemical methods. Consequently, the development of the appropriate additives and laser markable plastics is ongoing research. The laser-sensitive pigments^[12] such as mica, bismuth oxide (Bi_2O_3) and titanium dioxide (TiO_2) having ability to absorb laser energy and to induce chemical/physical changes are incorporated within the polymer matrix to improve the laser-marking performance, and produce well-defined and damage-free surface marks^[13-15].

Polybutylene terephthalate (PBT), an important engineering thermoplastic material, has played an important role in automotive, electronics appliances and precision instrument parts. The laser marking of PBT without adding laser sensitive pigments should be performed at a relatively high laser power, and the laser marking on the PBT surface obtained cannot be satisfying because the laser induced carbonization of PBT cannot be well-controlled, and the foaming can be generated easily, resulting in a poor laser marking quality including discontinuous lines, low contrast and sharpness of the mark.

In the present work, the SnO_2 particles of about $0.25\mu\text{m}$ were chosen to improve the laser marking performance of PBT. The used SnO_2 particles with particle size larger than the reported values of 6-8nm can absorb more laser energy, locally heat up and carbonize the surrounding polymer chains dramatically, which are probably equivalent to the core-shell particles obtained by the complicated modification of inorganic pigments

with polymers of high char residue. The PBT/SnO₂ materials were prepared by direct dispersing SnO₂ in PBT melt, and then marked by scanning with a controlled neodymium-doped yttrium aluminum garnet (Nd: YAG) pulsed laser beam at a wavelength of 1 064 nm in air. The laser induced markings of the PBT/SnO₂ materials and their suitability for the industrial use as the two-dimensional QR codes were studied under various marking conditions. The laser induced blackening of the PBT/SnO₂ material surfaces was investigated by using scanning electron microscopy (SEM), X-ray Diffraction (XRD), Raman spectroscopy, thermogravimetry analysis (TGA), and differential scanning calorimetry (DSC).

1 Experimental Section

1.1 Chemicals and Materials

Polybutylene terephthalate (PBT, 1100 A) with a melt flow index of 32.05g/10min (250°C/2.16kg) was supplied by Nantong Xingchen Synthetic Material Co., Ltd, China. Analytical grade stannic oxide (SnO₂) was obtained from the Tianjin-Fuchen Chemical Reagent Company, China. The average particle size of the SnO₂ particles was determined to be 249±73nm.

1.2 Preparation of PBT/SnO₂ sheet samples

PBT was dried in a ventilation oven at 120°C for 4h to remove water prior to use. The SnO₂ particles were mixed with PBT at a preset proportion in a high speed mixer. Mixtures of PBT and SnO₂ were obtained by mixing SnO₂ in PBT melt in a twin-screw extruder (CTE-35, Nanjing Machinery Co., Ltd, China) with a screw speed of 200r/min, feeding frequency of 4.0Hz and temperature profile ranging from 200°C to 240°C. The extrudate was cooled in a water bath at room temperature, dried, and granulated by pelletizer. The sheet samples for laser marking were injection molded by a plastics injection molding machine (CJ150, Zhende Plastic Machinery Co., Ltd, Chi-

na). A series of PBT/SnO₂ sheet samples were prepared and the loading mass contents of SnO₂ added to PBT were set to be 0, 1.0%, 2.0%, and 3.0%, respectively. The sheet samples obtained were labeled with the code 'PBT/SnO₂-SnO₂ content' (i.e. 'PBT/SnO₂-2.0%' refers to PBT/SnO₂ materials containing 2.0% SnO₂).

1.3 Instrumental and Characterization

Laser-marking experiments on the sheet samples were performed on a beam-controlled Nd: YAG laser-marking machine (KDD-50, Suzhou KiTe laser technology, China) at a wavelength of 1 064 nm. The focal length and spot size of the laser beam were 219mm and 100μm, respectively. The laser sweep speed was set as 450mm/s and the pulse repetition frequency was 4.0kHz. The laser beam was controlled by the software installed on the computer to design and create various marking symbols, and tune the laser parameters including laser power and laser scanning speed. The QR code mark was laser processed in a square area with side length of 2cm area, encoding the website of Changzhou University (<http://www.cczu.edu.cn>). The free QR code reader app installed on a smart phone was used to assess the readability of the QR codes marked on the samples at different laser powers.

The XRD patterns were characterized by a powder diffractometer (RINT2000, Rigaku) using Cu K_α X-rays with a wavelength of 0.154nm as the radiation source. The samples were characterized in a 2θ range from 5° to 70° at a scanning rate of 0.02° per second.

The Raman spectra of the PBT/SnO₂ sample surfaces before and after laser marking were collected on a DXR laser Raman spectrometer (Thermo Science and Technology Company) with a laser wavelength of 780nm, a laser power of 7mW and a slit width of 50μm.

Thermogravimetric analysis was carried out on 8mg samples using a NETZSCH-TG 209 F1 (NETZSCH, Germany) thermogravimeter at 20°C/min from 30 to 700°C under oxygen flow.

Thermal analysis was performed on a differen-

tial scanning calorimeter (Pyris8500, PerkinElmer, United States) in a nitrogen atmosphere and the gas flow rate was 20 mL/min. The mass of samples ranging from 3 mg to 6 mg were used. The samples were first heated at a rate of 20 °C/min from 10 °C to 260 °C, and remained at 260 °C for 3 min to erase thermal history. Then the sheet samples were cooled down at a rate of 20 °C/min to 10 °C, and subsequently held at 10 °C for 3 min. Finally, DSC thermograms and the thermal parameters were obtained when the samples were heated back to 260 °C at a rate of 20 °C/min, and remained at 260 °C for 3 min.

The morphology and structures of the surfaces and cross-sections of the samples before and after laser irradiation were observed using a metalloscope (ECLIPSE-LV150N, Nikon). SEM micrographs of SnO₂ particles, and surfaces of sheet samples before and after laser marking were recorded on a scanning electron microscope (JEOL, JSM-6360LA) at an acceleration voltage of 15 kV. A thin gold layer was deposited on the sample surface before SEM observation.

2 Results and discussion

2.1 Analysis of visual appearance of markings

A series of PBT/SnO₂ sheet samples were prepared by a facile method, which involved the direct dispersing different amounts of SnO₂ into PBT melt, and followed injection molding into sheets. Figure 1 shows visual appearance of markings including the laser power values employed, circles, and solid circles on the surfaces of PBT and PBT/SnO₂ (i.e. 1.0%, 2.0% and 3.0%) sheet samples after laser irradiation at different laser powers. Only slight surface change, vague characters and numbers were observed in the graph of the laser marked PBT sample obtained at low laser powers of 16.0 W and 21.0 W (see Fig. 1(a)). With the laser power increasing to 26.0 W and 31.0 W, the markings were becoming increasingly visible. However, low sharpness and contrast of the mark-

ings make PBT not suitable for commercial and industrial applications. After blending PBT with different amounts of SnO₂ additives, the black symbols and characters marked on PBT/SnO₂ sheet samples appeared in Figure 1(b), 1(c) and 1(d), of which marking quality depending on the loading content of SnO₂ and laser powers. The marking resolution and contrast are enhanced with the SnO₂ loading content increasing from 1% and 3%. This result indicated that the addition of laser sensitive SnO₂ particles can lead to high contrast marking of PBT at lower power, which is more effective and promising than the method of only increasing the laser power.

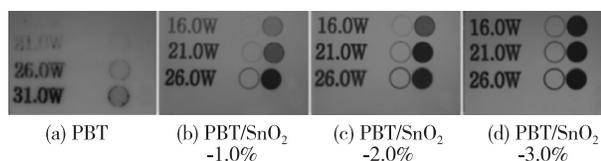


Fig.1 Visual appearance of markings on the surfaces of sheet samples after laser irradiation

The QR code as one type of two-dimensional barcode has been widely used for tracking and identification of products due to its fast readability and high storage capacity compared with the conventional barcodes. In order to examine the laser marking effect of pure PBT and PBT/SnO₂ materials and the suitability of these markings for the industrial use, the two-dimensional machine-readable QR code symbols were marked and studied for the PBT and PBT/SnO₂-2.0% sheet samples. From the appearance of the QR codes on the surfaces of the PBT and PBT/SnO₂-2.0% sheet samples in Figure 2, it was found that the addition of SnO₂ and the laser powers contributed to the marking contrast and quality. Deep blackness and high edge acuity of the QR code markings on the PBT/SnO₂-2.0% material surface were obtained at the laser power of 21.0 W. At laser power larger than 21.0 W, the reduced marking contrast and the rough surfaces were obtained for the composite sample due to the generation of white spots on surfaces accompanying the high degree of carbonization of the PBT polymer chains.

The white spots and rough surfaces were from foam generation during the decomposition reaction at high temperature and changes in the refractive index of the laser-marked layer under high laser power condition. Note that QR codes in this experiment were created to link to the website of Changzhou University (<http://www.cczu.edu.cn>). QR code symbols on PBT marked at 31.0W and PBT/SnO₂-2.0% sample marked at 16.0W cannot be recognized by the free QR code reader app installed on a smartphone due to their low marking quality and contrast. On the contrary, high contrast QR codes marked on the PBT/SnO₂-2.0% sheet samples at 21.0W and 26.0W can be quickly and easily read by the same QR code reader app, and the web browser can be launched to the designated website of Changzhou University. Therefore, the suitability of these markings for the industrial use as the two-dimensional machine-readable patterns has been confirmed.

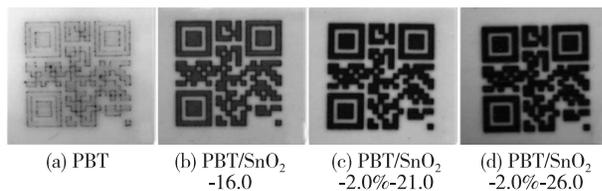


Fig.2 Laser induced QR codes on surfaces of samples

2.2 Analysis of metalloscope images

A metalloscope was employed to characterize the surfaces and cross-sections of the laser-marked PBT/SnO₂-2.0% and PBT/SnO₂-3.0% sheet samples at a laser power of 21.0W. As shown in Figure 3, the surface of the PBT/SnO₂-2.0% sample is relatively even after the laser-induced thermal chemical reactions, and the laser-marked area, which is much darker than the light-colored PBT substrate, exhibits high marking contrast. The depth of the mark on the PBT/SnO₂-2.0% sample after laser marking was about 172.83 μ m. However, from Figures 3 (b) and 3 (d), the surface of the PBT/SnO₂-3.0% sample became rather rough and seemed over-burnt, and the whole black carbonized layer has a thickness of a-

bout 306.53 μ m, which is 81.59 μ m thicker than the unmarked area. Compared with PBT/SnO₂-2.0% sample, the uneven and over-burnt area on the PBT/SnO₂-3.0% surface was due to more vigorous thermal-chemical reactions caused by more laser energy absorption of more SnO₂ particles per unit area of the composites, leading to the damaged PBT interface and low marking quality. In addition, the marking on the PBT/SnO₂-3.0% sample marked at a laser power of 21W is susceptible to wear and has poor durability, which is not suitable for industrial use.

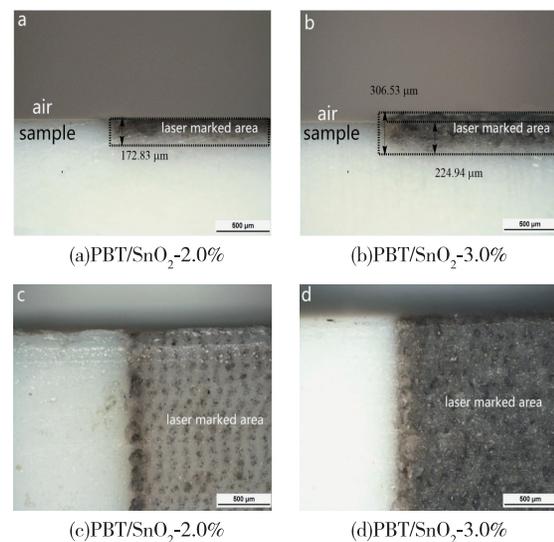


Fig.3 Metallographic images of surface and cross section samples after laser marking at a laser power of 21.0W

2.3 Analysis of SEM images

Compared with optical microscopy measurements, SEM examination can elucidate the changes in structures and morphologies of much smaller areas. Figure 4 shows the SEM images of the cross-sectional morphologies of PBT and PBT/SnO₂-2.0% samples before and after laser treatment. As shown in Figure 4(a) and 4(b), the SEM images demonstrated an obvious dispersion of SnO₂ in the continuous PBT matrix for the PBT/SnO₂-2.0% sample before laser treatment. After the laser marking at a laser power of 21.0W, the PBT/SnO₂-2.0% sample showed a relatively flat and damage-free surface, indicating the localized

heating by laser minimizing the thermal deformation. All the results for PBT and PBT/SnO₂ samples confirm that the addition of laser sensitive SnO₂ enables high contrast laser marking and damage-free surfaces of PBT after laser irradiation.

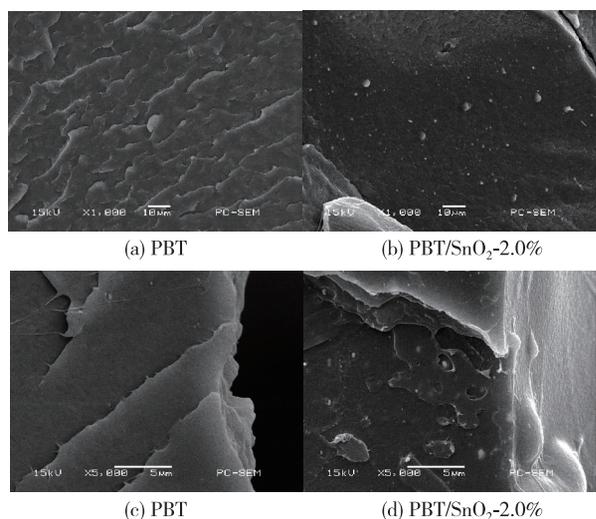


Fig.4 The SEM images of the cross-sectional morphologies of PBT and PBT/SnO₂-2.0% samples before and after laser treatment

2.4 Analysis of XRD patterns

To further explore the mechanism for the contrast of markings, the crystal structure and thermal properties of laser marked PBT/SnO₂ surface material were investigated. The PBT/SnO₂-2.0% sample was chosen for further characterization. Figure 5 shows the X-ray patterns of PBT/SnO₂-2.0% materials before and after laser marking at laser powers of 16.0W and 21.0W. As illustrated in Figure 5, several main reflections of the unmarked sample located at $2\theta = 15.8^\circ - 25.1^\circ$ and $2\theta = 26.5^\circ - 27.6^\circ, 33.6^\circ, 37.8^\circ, 51.7^\circ, 64.6^\circ - 65.8^\circ$ are belonging to the characteristic features of PBT and SnO₂, respectively. Compared with the unmarked sample, there are no new peaks observed in the X-ray patterns of the laser-marked PBT/SnO₂-2.0% samples at laser powers of 16.0W and 21.0W. Oujja et al^[12] revealed that the pigment vermilion was discolored due to the change of crystalline phase when irradiated using laser pulse at 1064nm. However, this re-

sult shows that the crystal form of the marked surface material has not been changed, indicating that the generation of black-colored mark is attributed to the amorphous carbonized PBT material. During the process of laser marking, it can be also concluded that the function of SnO₂ is to absorb laser energy and to heat the surrounding polymer chains while the crystal structure of SnO₂ remains unchanged.

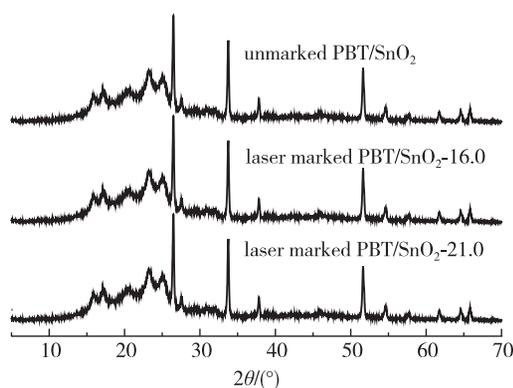


Fig.5 XRD patterns of PBT/SnO₂-2.0% material samples before and after laser marking

2.5 Analysis of Raman spectra

Raman spectroscopy is adopted to confirm the structure and composition of the amorphous carbon materials probably formed during the laser marking. It is reported in the literature that a broad diffusion band assigned to the characteristic band of amorphous carbon is present at about 1580cm^{-1} ^[16]. Raman spectra of the unmarked and marked PBT/SnO₂-2.0% material samples at laser powers 16.0W and 21.0W are displayed in Figure 6. The characteristic band of amorphous carbon was not observed for the unmarked sample due to the simple mixing of PBT with SnO₂ prior to laser marking. On the contrary, a broad diffusion band in the range from 1000 to 2000cm^{-1} appeared in the Raman spectra of the laser-marked PBT/SnO₂-2.0% materials, which is assigned to amorphous carbon. In addition, a high laser power can lead to an increased intensity of the amorphous carbon band due to the laser-enhanced carbonization. These results are in good agreement with the

Raman data reported by Zhong et al in which the laser marked TPU/Bi₂O₃ materials showed the similar band of the amorphous carbon in the same range from 1 000 to 2 000 cm⁻¹[15]. The intensity of four bands at around 1 614 cm⁻¹, 1 717 cm⁻¹, 1 453 cm⁻¹, and 1 278 cm⁻¹, which were present in the spectrum of unmarked sample, was found to decrease in the spectra of laser-marked samples. This can be explained that absorption of laser light energy by SnO₂ particles leads to thermal decomposition (pyrolysis) of the PBT chains surrounding the overheated particles. PBT chains in PBT/SnO₂-2.0% material partially underwent pyrolysis and carbonization, and the main characteristic peaks of PBT chains still existed after laser marking. Nevertheless, the intensity of characteristic PBT peaks greatly decreased due to the formation of the amorphous carbonized material. Therefore, the formation of the distinct black marking on the PBT/SnO₂ surface after laser irradiation was due to the local carbonization via PBT pyrolysis.

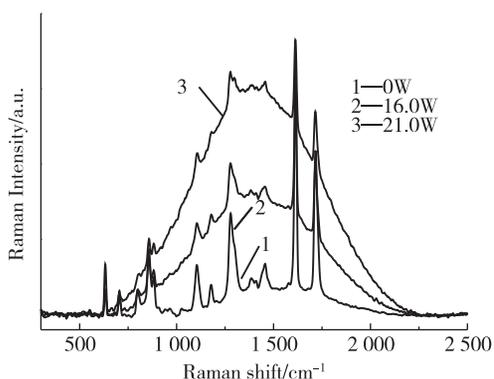


Fig. 6 Raman spectra of the PBT/SnO₂-2.0% material samples before and after laser marking

2.6 Analysis of TGA curves

To verify the laser induced pyrolysis of the PBT chains, the TGA curves (Figure 7) of the PBT/SnO₂-2.0% samples were measured in oxygen before and after laser marking at laser powers of 16.0 and 21.0W. Table 1 summarizes the characteristic TGA results of the PBT/SnO₂-2.0% material samples before and after laser marking. The unmarked PBT/SnO₂-2.0% sample

showed the five percent weight loss ($t_{5\%}$) and ten percent weight loss ($t_{10\%}$) at about 321.6°C and 341.8°C, respectively. However, $t_{5\%}$ and $t_{10\%}$ of the PBT/SnO₂-2.0% sample marked at a laser power of 16.0 W were found to be 315.8°C and 336.7°C. With increasing the laser power from 16.0W to 21.0W, the laser-marked samples had lower $t_{5\%}$ and $t_{10\%}$ values of 309.9°C and 331.9°C. The $t_{5\%}$ and $t_{10\%}$ of unmarked materials were slight higher than those of the laser-marked materials. Besides, the unmarked PBT/SnO₂-2.0% sample showed the first degradation peak (t_{max1}) at approximately 397.3°C, which is higher than t_{max1} values of 396.6°C and 395.2°C of the laser marked samples. This result shows that the thermal stability of the PBT/SnO₂-2.0% material after laser marking decreased, which is attributed to the pyrolysis of surface PBT chains induced by laser irradiation, thus decreasing both the onset and the maximum weight loss temperatures of the composites. It can be also concluded that the higher laser power leads to more vigorous thermal degradation of PBT chains.

Table 1 Characteristic TGA data of the PBT/SnO₂-2.0% material samples before and after laser marking

Samples	$t_{5\%}/^{\circ}\text{C}$	$t_{10\%}/^{\circ}\text{C}$	$t_{max1}/^{\circ}\text{C}$
PBT/SnO ₂ -2.0%	321.6	341.8	397.3
PBT/SnO ₂ -2.0%-16.0	315.8	336.7	396.6
PBT/SnO ₂ -2.0%-21.0	309.9	331.9	395.2

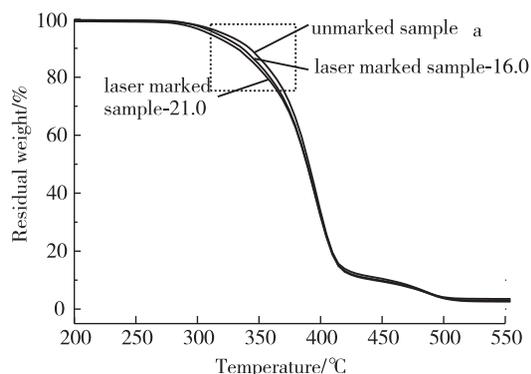


Fig. 7 TGA curves of the PBT/SnO₂-2.0% samples before and after laser marking

2.7 Analysis of DSC thermograms

DSC thermograms and the thermal parameters of the PBT/SnO₂-2.0% material samples before and after laser marking at laser powers of 16.0W and 21.0W are shown in Figure 8 and Table 2, respectively. In Figure 8, the unmarked PBT/SnO₂-2.0% sample shows one single melting peak at around 224.9°C, which is assigned to the characteristic feature of PBT crystalline structure. Compared with the unmarked sample, the PBT/SnO₂-2.0% material samples marked at 16.0W show the double melting peaks at approximately 217.7°C and 224.2°C. The new peak at lower melting temperature (t_{m1}) should be attributed to the formation of crystal grains of lower molecular weight PBT produced during the pyrolysis induced by laser marking. The same double melting peaks were also found in the thermograms of PBT/SnO₂-2.0% sample laser marked at 21.0W. Roland et al. studied the thermal marking of amorphous PET film by a CO₂ laser, and the crystallization and melting of PET were observed during the heating process induced by laser irradiation, depending on the intensity of the laser radiation^[17]. As shown in Table 2, the enthalpy of melting (ΔH_m) of the unmarked PBT/SnO₂-2.0% material samples is higher than those of the laser marked ones. Furthermore, with increasing the laser power from 16.0W to 21.0W, the ΔH_m of PBT/SnO₂-2.0% material sample was reduced slightly from 46 to 45J/g. Because the polymer chains experiencing degradation in PBT/SnO₂ materials was accounting for a relatively small proportion during the laser marking, so the variation in this value is not too high. This result illustrates that the crystallinity of the PBT/SnO₂-2.0% material is decreased after laser irradiation, which is attributed to the pyrolysis of surface PBT chains, and more vigorous pyrolysis occurs at the higher laser power. The DSC results further confirmed the explanations regarding the pyrolysis of PBT chains induced by laser irradiation that were established by optical microscopy, SEM, Raman

spectroscopy, and TGA. Therefore, a mechanism for the laser-induced marking of PBT/SnO₂ materials can be proposed. The SnO₂ particles dispersed in the PBT matrix can absorb laser energy and heat the surrounding PBT matrix, leading to the local carbonization of polymers, and hence the generation of black-colored marks on the surface.

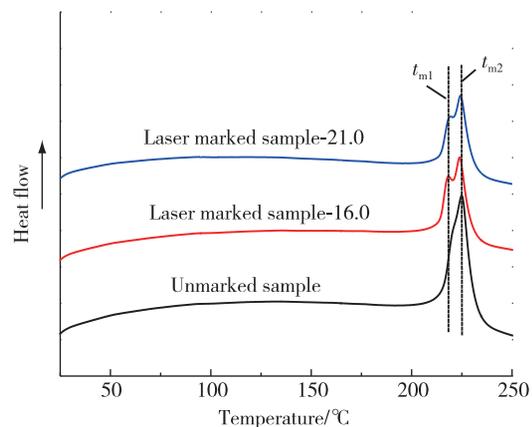


Fig.8 DSC thermograms of the PBT/SnO₂-2.0% samples before and after laser marking

Table 2 Thermal parameters of the PBT/SnO₂-2.0% material samples before and after laser marking

Samples	$t_{m1}/^{\circ}\text{C}$	$t_{m2}/^{\circ}\text{C}$	$\Delta H_m/(\text{J/g})$
PBT/SnO ₂ -2.0%	—	224.9	57.1
PBT/SnO ₂ -2.0%-16.0	217.7	224.2	46.0
PBT/SnO ₂ -2.0%-21.0	218.2	224.6	45.0

3 Conclusions

Optical microscopy, SEM, XRD, Raman spectroscopy, TGA, and DSC demonstrated that the high contrast markings including two-dimensional machine-readable codes can be easily produced on surfaces of PBT by simple mixing with SnO₂, and followed by a laser irradiation procedure. The laser marking of pure PBT requires a high laser power, leading to low quality marks with low edge-sharpness and high roughness. PBT with the addition of SnO₂ as a laser sensitive component can achieve high-quality marks on its surface, of which marking contrast and visual appearance are dependent on the SnO₂ loading amount and laser power. The high contrast two-dimensional machine-readable codes can be

produced on the surface of the PBT/SnO₂ material samples added with 2% SnO₂ and marked at a laser power of 21.0W. The absorption of laser light energy by the SnO₂ particles leads to thermal decomposition (pyrolysis) of the PBT chains surrounding the overheated particles. The formation of distinct black marking on the PBT/SnO₂ material surface after laser irradiation was due to the local carbonization via PBT pyrolysis without changing the crystal structures of SnO₂. The facile preparation of laser marking PBT/SnO₂ materials and the easy marking of high contrast two-dimensional machine-readable marks on their surfaces are promising for the identification and decoration purpose of PBT products.

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