Surface Laser-Marking and Mechanical Properties of Acrylonitrile-Butadiene-Styrene Copolymer Composites with Organically Modified Montmorillonite

Guangwei Lu, Yinqiu Wu, Yang Zhang, Kailun Wang, Hongxin Gao, Keming Luo, Zheng Cao,* Junfeng Cheng, Chunlin Liu, Lei Zhang, and Juan Qi

ABSTRACT: In this study, organically modified montmorillonite (OMMT) was prepared by modifying MMT with a cationic surfactant cetyltrimethylammonium bromide (CTAB). The obtained OMMT of different loading contents (1, 2, 4, 6, and 8 wt %) was melt-blended with poly(acrylonitrile-co-butadiene-co-styrene) (ABS) to prepare a series of ABS/OMMT composites, which were laser marked using a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser beam of 1064 nm under different laser current processes. X-ray diffraction (XRD), color difference spectrometer, optical microscope, water contact angle tests, scanning electron microscope (SEM), and Raman spectroscopy were carried out to characterize the morphology, structure, and properties of the laser-patterned ABS composites. The effects of the addition of OMMT and the laser marking process on the mechanical properties of ABS/OMMT composites were investigated through mechanical property tests. The results show that the obtained ABS/OMMT composites have enhanced laser marking performance, compared to the ABS. When the OMMT content is 2 wt % and the laser current intensity is 9 A, the marking on ABS composites has the highest contrast \( \Delta E = 36.38 \) and sharpness, and the quick response (QR) code fabricated can be scanned and identified with a mobile app. SEM and water contact angle tests showed that the holes, narrow cracks, and irregular protrusion are formed on the composite surface after laser marking, resulting in a more hydrophobic surface and an increased water contact angle. Raman spectroscopy and XRD indicate that OMMT can absorb the near-infrared laser energy, undergo photo thermal conversion, and cause the pyrolysis and carbonization of ABS to form black marking, and the crystal structure itself does not change significantly. When the 2 wt % of OMMT is loaded, the tensile strength, elongation at break, and impact strength of ABS/OMMT are increased by 15, 20, and 14%, respectively, compared to ABS. Compared with the unmarked ABS/OMMT, the defects including holes and cracks generated on the surface of the marked one lead to the decreased mechanical property. The desirable combination of high contrast laser marking performance and mechanical properties can be achieved at an OMMT loading content of 2 wt % and a laser current intensity of 9 A. This research work provides a simple, economical, and environmentally friendly method for laser marking of engineering materials such as ABS.

1. INTRODUCTION

ABS, a thermoplastic engineering plastic, is widely used in automotive, the electronics industry, outdoor advertising, 3D printing, and other fields\(^1\)\(^-\)\(^4\) due to its good mechanical properties, chemical resistance, easy molding, and processing characteristics. In the field of household appliances, the surface of ABS needs to be marked with text and patterns to indicate the company’s logo, production serial numbers, and anti-counterfeiting functions. Generally texts or patterned marks are fabricated on the material surface through ink printing, but there is the use of toxic organic solvents and chemicals and poor marking wear resistance.\(^5\)\(^,\)\(^6\) Therefore, there is an urgent need for a fast, efficient, and cost-effective marking method for ABS.

Laser marking technology has been widely used in the marking and patterning of material surfaces due to its rapid, efficient, and environmentally friendly advantages.\(^7\)\(^-\)\(^13\) Due to the wide variety of polymer materials having different structures and compositions, their laser response performance and the clarity and contrast of laser marking also show...
Abs has excellent chemical stability and mechanical properties, but ABS is not a very good absorber of the near-infrared laser, leading to the blurred laser marking.\(^\text{14}\) Research and development of simple, convenient, low-cost, and environmentally friendly ABS laser marking materials for its application is very important. From many studies,\(^\text{15−20}\) it is observed that polypropylene (PP)-, polyethylene (PE)-, and polyacrylamide (PAM)-based hydrogel materials are insensitive to the near-infrared laser with 1064 nm wavelength, difficult to absorb laser energy, and cannot produce high definition and contrast laser marking text and patterns. In order to solve the problem of poor absorption of the near-infrared laser by such materials, laser-sensitive inorganic particles, such as graphene, multilayer graphene,\(^\text{21}\) tin dioxide,\(^\text{20}\) antimony (III) oxide,\(^\text{23}\) bismuth oxide,\(^\text{22}\) magnetic particles,\(^\text{26}\) carbon nanotubes,\(^\text{27}\) etc., are introduced into the polymer materials and can effectively absorb near-infrared laser energy and convert it into heat, resulting in polymer carbonization or formation of foam, which contributes to the black or light markings on the material surface. For example, Zhang et al.\(^\text{26}\) prepared a series of thermoplastic polyurethane (TPU) composites with iron oxide and zirconium oxide (Fe\(_3\)O\(_4\)/ZrO\(_2\)) as laser-sensitive particles by melt blending and found that Fe\(_3\)O\(_4\)/ZrO\(_2\) nanoparticles could absorb laser energy, the melting and pyrolysis of the TPU chain at high temperature occurred, and the generation of gaseous products led to the formation of high contrast and light-color markings on the black TPU surface. Zhou et al.\(^\text{27}\) reported the use of carbon nanotubes for improving the laser pattern performance of PP. The three-dimensional network structure formed by CNTs can effectively improve the photothermal conversion effect of PP/CNT composite materials. The results show that the addition of 10 ppm CNT gives PP a clear black laser pattern performance. This simple method of adding inorganic laser-sensitive particles into polymers is highly attractive and easy to implement and can solve the problem of poor sensitivity of polymer materials to near-infrared lasers.

However, some inorganic particles, such as bismuth- and arsenic-containing oxides, are highly toxic and easy to leak from resin, which is harmful to the environment and human health. Carbon nanotubes and graphene oxide are not easy to prepare and very expensive, affecting large-scale industrial applications. Most literature studies have revealed that although inorganic particles can improve laser marking performance, the effects of incorporation of particles and the laser marking process on the mechanical properties of materials have not been reported yet. It is generally believed that inorganic particles in the substrate resin are not well dispersed, leading to aggregation of particles and incompatibility between inorganic particles and the polymer substrate, thus affecting the mechanical properties of the material.\(^\text{28−32}\) Therefore, it is still necessary to find inorganic particles with rich sources and cost-effective, environmentally friendly, and good laser-sensitive features for the design and preparation of polymeric composites with both improved laser marking and mechanical properties.

MMT is an inorganic clay material, with the unique layer-shaped one-dimensional nanostructure properties, a designable layer reactivity, large surface area, and good cation exchange capacity.\(^\text{33,34}\) Because of the advantages including the excellent mechanical properties, gas barrier and flame retardant performance, low cost, and processing convenience, MMT has been widely used in textile, adsorption materials, coatings, pharmaceuticals, and other industries.\(^\text{35−41}\) Duchek et al.\(^\text{42}\) studied the structural and performance changes of MMT after the infrared laser irradiation and found that the laser-induced process led to the complete amorphization of MMT particles and different morphologies depending on the laser energy. This laser-induced property will be helpful for making clay nanocomposites and nanostructure clay films. We propose to introduce MMT as a laser-sensitive additive into ABS and to study the laser marking properties of ABS composites after the laser irradiation. Because the basal space of MMT is about 1 nm and the chemical environment between the layers is hydrophilic and oil-repellent, it is rather difficult for polymers and organic molecules to be intercalated into MMT. The composite materials that are simply mixed in this way become brittle and do not have good mechanical properties. Therefore, for the preparation of the organic/inorganic nanocomposites with excellent performance, clay modification is a very important step. The commonly used modifiers include alkyl quaternary ammonium salts,\(^\text{43}\) polymer,\(^\text{44−46}\) and coupling agent,\(^\text{47}\) which can be intercalated into MMT via chemical adsorption, ion exchange, and so on.

In this study, the silanes and CTAB were chosen for organically modifying MMT. The organically modified MMT (OMMT) with the largest basal spacing value would be incorporated into ABS by melt blending, which not only improves the mechanical properties of ABS but also opens up new ways for laser marking of polymers. Until now, there have been no reports of the use of OMMT as a laser-sensitive particle to improve the laser marking performance of ABS.
This research aims to improve the laser marking performance of ABS by simple melting with low cost and environmentally friendly OMMT. ABS/OMMT composite samples were characterized with visual observation, a color difference spectrometer, an optical microscope, water contact angle measurements, XRD, SEM, and Raman spectroscopy. The mechanical properties of ABS/OMMT composites before and after laser marking were also investigated. ABS/OMMT composite materials with a desirable combination of laser marking performance and mechanical properties were finally prepared.

2. RESULTS AND DISCUSSION

Figure 1 shows the illustration of the first modification of MMT (taking CTAB for example), then the preparation of the ABS/OMMT composites, and the final laser marking process. First, MMT was organically modified with the cationic surfactant CTAB, silane, and titanate coupling agents as modifiers, respectively. For example, the alkyl ammonium ions of CTAB can be intercalated into MMT through the ion-exchange reaction, and the surface of the layer is covered by the alkyl long chain, thus changing the surface from hydrophilic to hydrophobic, which is conducive to enhancing the compatibility of MMT and the polymer ABS substrate. Silane and titanate coupling agents are chemically reacted with the hydroxyl groups on the surfaces of MMT particles, thus covering the surface of MMT, ensuring that the particles are dispersed evenly in the polymer substrate for modification purposes. Through the analysis of the modified effect of the different modifiers, we hope to obtain the modified MMT with the largest basal spacing, mix it with ABS in different proportions, and finally prepare a series of ABS/OMMT composites by means of mechanical shear and melting. The surface marking of ABS/OMMT composite materials is performed using a beam controlled Nd:YAG laser at 1064 nm. By controlling the laser current intensity and the loading OMMT content, it is expected to obtain the ABS/OMMT composites with the desirable combinations of laser marking performance and mechanical properties.

Figure 2 shows the FT-IR spectra of pure MMT and modified MMT with KH550, KH570, titanate coupling agents, and the cationic surfactant CTAB, respectively. It can be seen from Figure 2a that a broad band at 3650–3250 cm\(^{-1}\) is attributed to the stretching vibration of hydroxyl groups on the surface of MMT, and the absorption band at around 1030 cm\(^{-1}\) is the stretching vibration of Si–O–Si in MMT. The band at 600–500 cm\(^{-1}\) is ascribed to the bending vibration of Al–O and Si–O in MMT. It can be seen from Figure 2b–d that FT-IR spectra of MMT modified with KH550, KH570, and titanate coupling agents, compared with pure MMT, show two additional peaks at around 2930 and 2840 cm\(^{-1}\), which correspond to the stretching vibration absorption of C–H groups and indicate the chemical bonding of the coupling agent on the surface of MMT. Compared with the FT-IR spectrum of MMT, several absorption bands at around 2930, 2840, and 1470 cm\(^{-1}\), belonging to the characteristic C–H absorption of the organic alkyl groups,\(^{48}\) could be observed in the FT-IR spectrum of CTAB-modified MMT. This is because the alkyl ammonium ions of CTAB can be intercalated into MMT via ion exchange. This result clearly indicates that the organic modification of MMT can be achieved with the cationic surfactant CTAB.

Table 1. XRD Data for MMT and the Modified MMT with KH550, KH570, Titanate Coupling Agents, and the Surfactant CTAB

| samples        | 2θ (°) | basal (001) space (nm) |
|----------------|--------|------------------------|
| MMT            | 7.78   | 1.11                   |
| KH550-MMT      | 4.86   | 1.82                   |
| KH570-MMT      | 4.56   | 1.94                   |
| TSL-MMT        | 4.86   | 1.82                   |
| CTAB-MMT       | 4.42   | 2.00                   |

Figure 3 shows the XRD patterns of pristine MMT and the modified MMT with KH550, KH570, titanate coupling agents, and the surfactant CTAB.
angle of the diffraction peak, the basal spacing of MMT and the modified MMT layers can be calculated using Bragg’s law. The basal spacings of 1.11, 1.82, 1.94, 1.82, and 2.00 nm are obtained for MMT and the modified MMT with KH550, KH570, titanate coupling agents, and CTAB, respectively. Compared to pristine MMT, the basal spacing of the organically modified MMT was increased. Typically, silane conjugates and titanate molecules react with hydroxyl groups through hydrolysis and condensation and enter into the MMT interlayer, resulting in an increase in the basal spacing of MMT layers. Unlike silane coupling agents, CTAB is a surfactant that increases layer spacing by exchanging ions between the cations and the alkyl ammonium ions. The organic cations of CTAB can change the surface of MMT from hydrophilic to hydrophobic, reducing the surface energy of the MMT surface and improving its compatibility with polymer substrates and monomers. Compared with the alkyl ammonium ions, the alkyl chain of the silane coupling agent is shorter, so the improvement of basal spacing is not obvious. Through the analysis of the above experimental results, the CTAB-modified MMT was chosen for adding into ABS, the ABS/OMMT composite was prepared, and its laser marking performance was investigated.

Figure 4 shows the visual appearance of the laser pattern (solid square) on ABS and ABS/OMMT composites with different OMMT loading contents from 1 to 8 wt % after laser marking at different current intensities from 7 to 11 A. As can be seen from Figure 4, under the lower current intensity of 7 A, ABS cannot be marked with a near-infrared laser, showing several black spots and no obvious carbonization phenomenon. As the laser marking current intensity increases to 8 A, the surface of ABS displays many black points and a vague marking pattern. When the laser marking current intensity is increased to 9 A, a clear marking pattern of solid squares with increased blackness and a sharper edge is shown. At the higher laser current intensity of 10 and 11 A, it is found that a more obvious black square marking pattern appears on the ABS surface. However, the high laser energy leads to the locally overheating, carbonization, and obvious foaming of ABS. The uneven surface produced affected the appearance of the material and reduced the use value. At the lower current intensity, absorption of near-infrared laser energy is not enough for ABS, resulting in a poor laser marking effect. By simply increasing the laser current intensity, although the clarity of the ABS surface pattern can be improved, it will also produce local overheating and cause material degradation and foaming. Increasing the laser current intensity is not an ideal method. Therefore, the introduction of the organically modified OMMT in ABS material will be a better choice. With the loading of OMMT, the obtained ABS/OMMT composites marked at different laser current intensities showed the enhanced laser marking performance, compared to ABS. With only 1 wt % OMMT added, a clearer pattern can be formed when marked at a laser current intensity of 7 A. As the current intensity increases, the pattern becomes clearer and remains stable after 9 A. Similarly, the laser marking pattern with high clarity and contrast can be observed for ABS composites with a higher OMMT content of 2, 4, 6, and 8 wt %. These phenomena can be interpreted as the ability of the intercalated layer with CTAB to absorb the energy of the near-infrared laser and transform the light into heat. ABS chains surrounding the OMMT particles undergo pyrolysis and carbonization at a high temperature, forming a black laser marking pattern. With the increase of the OMMT loading content and the laser current intensity, a more intense photothermal reaction occurs at the elevated temperature, resulting in carbonization and black marking with different clarities and contrasts. By comparing the visual appearance of various ABS composites obtained, it can be found that the laser current intensity of 9 A plays an important role in the laser marking process. Considering that it is better to obtain the clear laser patterns at the laser current intensity as lower as possible and save energy from the economic point, the following research will continue to examine the relationship between the marking pattern performance and the loading OMMT content under the same laser marking current of 9 A and the effect of the OMMT content on the appearance and surface morphology of the laser-marked ABS composites.

Figure 5 shows the visual appearance of the laser pattern (solid square) and text (ABS) of ABS and ABS/OMMT composites with various OMMT loading contents of 1, 2, 4, 6, and 8 wt %, respectively. As can be seen from Figure 5, a vague black square pattern and text “ABS” appear on the ABS surface. Only the edge of “ABS” is obviously visible, and the inside of the text is hollow. With the increase of the OMMT loading content from 1 to 2 wt %, a deep black solid square and clear text with sharp edges are shown on the surface of the ABS composites. As the loading content of OMMT further
increased from 4 to 8 wt %, the blackness of the square black marking was found to increase, but the color contrast with the substrate decreased, especially as the text “ABS” became blurred and the clarity and contrast decreased further. Because OMMT is a pigment, with the increase of the OMMT content, the color of ABS resin becomes darker, resulting in a decreased contrast of the marking pattern on the ABS matrix. In addition, at the same laser current intensity of 9 A, a high content of OMMT can absorb more laser energy and produce more heat, and the surface of the ABS composite is more prone to foam and becomes uneven. Considering that when used as a laser-sensitive additive, OMMT should not affect the visual appearance and properties of the substrate material, the ABS composite material with 2 wt % OMMT is selected for the following study.

In order to observe the pattern of laser marking in more detail, an optical microscope was used to characterize the ABS/OMMT composites. Figure 6 shows optical microscope observation of laser patterns on ABS and ABS/OMMT composites loaded with different OMMT contents including 1, 2, 4, 6, and 8 wt % (dotted line indicates the edges of the laser-marked patterns). As shown in Figure 6, for ABS, after the laser marking under a laser current intensity of 9 A, the pattern was composed of small black spots with different sizes, and the edge of the marking pattern (see the dotted line in Figure 6) is not flat and similar to ripples, which causes the formation of the blurred and unrecognizable patterns, that is, the laser marking pattern is not controllable. At 1 wt % of the OMMT content, it can still be seen that the laser pattern was made up of the small black spots with a similar size, and the pattern edge is still not so sharp. When the OMMT content continues to increase to 2 and 4 wt %, the laser-marked pattern of ABS composite materials has a darker surface, sharper contours at the edges, and increased pattern contrast. As the OMMT content increased to 6 and 8 wt %, laser patterns with a lower contrast were observed for ABS composites. OMMT is a pigment that fills into polymers to cause the substrate to turn yellow. When observed under an optical microscope, ABS composites with 6 and 8 wt % OMMT have a dark background, and the contrast between the black markings and the light substrate material decreases. Although the markings are darker, the substrate material also turns dark, and the markings are not clear visually. In order to more quantitatively characterize the contrast changes of laser marking patterns on the surface of ABS composite materials with the addition of OMMT, the color difference tests were carried out to reduce the error of visual observation.

Figure 7 shows a $\Delta E$ value of the surface marking patterns of ABS/OMMT composites marked at different laser marking current intensities (7, 8, 9, 10, and 11 A) as a function of the OMMT content (the QR code marking pattern is inserted). As can be seen from Figure 7, without loading OMMT, as the laser marking current intensity varies from 7 to 11 A, a $\Delta E$ value of the surface marking on ABS changes from 0.5 to 17.0. When the different loading contents of OMMT are added, the $\Delta E$ value of the marked pattern of the resulting ABS composites significantly increased at the same current intensity, compared to ABS. When the laser marking current intensity is 7 A, with the increase of the OMMT content from 1 to 8 wt %, the $\Delta E$ value of laser marking on the ABS composite increased from 7 to 25, indicating that OMMT can play a role in absorbing near-infrared laser energy and photothermal transformation, leading to the degradation of the ABS chain and formation of a carbonized black marking. At the same OMMT content, the $\Delta E$ value of ABS composite materials increases accordingly as the laser marking current.
intensity increases from 7 to 9 A. The greater the laser marking current intensity, the more the energy of the laser radiation and the more intense the OMMT photothermal reaction, resulting in a higher carbonization and better laser marking performance. However, when the laser marking current is 9 A, with the change of the OMMT content, the ΔE value of surface markings reaches the maximum value of 36.38 at an OMMT content of 2 wt %. This result is consistent with the one of Figures 5 and 6, and more OMMT additions will lead to darkening of the ABS substrate, resulting in a decrease in the contrast of the final laser marking pattern. When the laser current intensity is 10 and 11 A, the ΔE value of ABS composites with various OMMT contents does not increase significantly but decreases slightly, compared to that obtained at a laser intensity of 9 A. This result shows that a high laser current intensity does not further improve the contrast of the laser marking, which is in agreement with the observation in Figures 5 and 6. Because a high laser marking current intensity leads to the severe degradation of ABS chains and the production of bubbles, a rough surface and slight decreased laser marking contrast were obtained. Through the above analysis, the ABS composite with the highest contrast and clarity can be obtained at 2 wt % OMMT and a laser marking current intensity of 9 A. Under this condition, a laser-marked QR code is created, can be identified with the mobile phone APP, and connected to the web site of www.cczu.edu.cn (see the inserted QR code in Figure 7).

Figure 8 shows SEM images of the surface morphology of ABS/2%OMMT composites at the laser current intensities of 8 and 9 A. It can be seen from Figure 8a that the surface of the unmarked area of the ABS composite is flat and the surface roughness is rather low. When the laser marking current intensity is 8 A, compared to the unmarked areas, the surface of the marked area has a large number of depressed holes and irregular protrusions. This phenomenon indicates the role of OMMT filled in the ABS resin. During the laser marking process, OMMT can absorb the laser light energy at a wavelength of 1064 nm and undergo the serious photothermal conversion, leading to the physical and chemical changes including pyrolysis, carbonization, melting, and resolidification of ABS chains surrounding the inorganic particles. Therefore, a number of holes and irregular protrusions were formed on the surfaces after laser-induced irradiation. There is a clear boundary observed between the marked area and the unmarked area, which is indicated with dotted lines (see Figure 8a). During the laser marking process, the black marking on the light substrate was fabricated on the surfaces of the ABS composites due to the generation of the dark carbonized materials. From Figure 8b, it can be observed that the surface of the marked area of the composite material shows distributed holes, and the hole size is about 60–125 μm (see the details in the circle). With a larger magnification, as shown in Figure 8c, the holes have a certain depth, and the irregular internal structure was formed due to the melting, pyrolysis, and carbonization of the ABS matrix at the local high temperature induced by the photothermal reaction of MMT after laser marking. At a higher laser marking current of 9 A, as shown in Figure 8c–e, deep internal holes with an increase size of 95–230 μm after laser marking and more narrow cracks and irregular protrusions were observed, indicating pyrolysis and carbonization processes caused by more intense photothermal reactions. The surface morphology and structure after laser marking are greatly dependent on the laser marking current intensity. An internal porous structure containing more small
particles formed at 9 A can be clearly observed, compared to the counterpart of the one at 8 A. It can be seen that the surface properties and morphology of ABS/OMMT composites have changed greatly. The holes and narrow cracks that appear after marking have also caused the surface roughness to change, influencing the hydrophilic and hydrophobic properties of the material surface. It is possible to estimate that the presence of holes and narrow cracks formed on the surfaces could lead to the decrease in the stability and reliability of the ABS/OMMT composites. The following study will further analyze the change in the surface water contact angle, and Figure 9 shows the change in the water contact angle of the ABS and ABS/2%OMMT composites before and after laser marking. As can be seen from Figure 9a,b, the water contact angle values of ABS before and after marking at a laser current intensity of 11 A are 71° and 76°, respectively. This shows that higher laser energy causes the surface morphology of ABS to change, and the surface roughness and the water contact angle increase slightly. From Figure 9c−e, it can be observed that the water contact angle of the surface of the ABS/2% OMMT composite material before laser marking is 81.5°. At the laser marking current intensities of 7 and 11 A, the water contact angle becomes 86° and 116.5°, indicating the enhanced hydrophobic property on the surface. This is attributed to the role of OMMT in ABS laser marking, that is, absorbing laser energy and undergoing the photothermal reaction, leading to the pyrolysis and carbonization of ABS chains at the high temperature. After laser marking, holes and narrow cracks were formed, and the irregular protrusions on the surface and the roughness increased, resulting in an increase in the water contact angle. This result is consistent with the results reported by Li et al. They studied the changes in the morphology and wettability of the aluminum alloy surface after laser marking and found that by laser marking, the microstructure with irregular protrusions and pits on the surface of the aluminum alloy showed superhydrophobic properties. Consistent with the report in the literature, after laser marking, a large number of grooves and irregular protrusions were generated on the surface of the ABS/OMMT composites, which caused the contact angle to increase and showed superhydrophobic properties. Through the above analysis, the surface of the ABS/OMMT composite material was carbonized under the action of the laser, and many small cracks and holes and irregular protrusions were formed on the surface,
which caused the contact angle of the material to increase. As the laser current intensity increased, the number of cracks on the surface will increase rapidly, which will increase the contact angle rapidly. This feature can be considered for making superhydrophobic materials. However, the number and size of surface cracks relating the surface damage will increase with the increase of laser current intensity. This makes it better to laser mark composite materials at lower and medium intensity currents, that is, to choose a suitable laser marking current intensity because the high intensity current intensity is most likely to cause the surface damage, which will probably affect the mechanical properties of the material.

In order to clarify the mechanism of laser-induced blackening of ABS/OMMT composite materials, the material before and after marking is analyzed by Raman spectroscopy. Raman spectroscopy is an effective method for studying the structure and properties of carbon materials such as graphene. Different carbon materials and their corresponding carbon structures exhibit different characteristic bands in their Raman spectra. The laser-induced blackening of polymers due to the formation of the black carbonized materials can be confirmed by Raman spectroscopy. Figure 10a shows Raman spectra of ABS and ABS/2% OMMT composites before and after laser marking. Compared with ABS and unmarked ABS/OMMT composites, the laser-marked ABS/OMMT composite showed a wide amorphous carbon band in the range of 1000–1500 cm$^{-1}$. This result indicated that OMMT incorporated can effectively absorb the energy of the near-infrared laser and undergo the photothermal reaction. The produced locally high temperature leads to the thermal pyrolysis and carbonization of the ABS chain, and a black marking pattern can be formed on the surface. This observation is consistent with the results reported in the literature that after laser marking, TPU/Bi$_2$O$_3$ and PP/Sb$_2$O$_3$ composites will produce a broad diffusion band in the range of 1000–2000 cm$^{-1}$ assigned to the amorphous carbon.

In order to better verify whether the OMMT laser-sensitive additives have changed the crystal structure after the laser marking, XRD is used to characterize the ABS and ABS/OMMT composites before and after laser marking (see Figure 10b). As can be seen from Figure 10b, no changes have been found in the XRD patterns of ABS before and after the laser marking. Compared with ABS, the unmarked ABS/OMMT composites show several characteristic diffraction peaks, such as one peak at 2$\theta$ = 25°, which is attributed to the presence of OMMT crystalline structures. After laser marking, the XRD

Figure 11. Mechanical properties of ABS/MMT, unmarked ABS/OMMT, and marked ABS/OMMT composite materials (laser marking current intensity of 9 A) including: (a) tensile strength, (b) elongation at break, and (c) impact strength.
pattern of the marked ABS/OMMT composite was consistent with the unmarked one, and no new XRD diffraction peaks were found. This result shows that OMMT plays the role of absorbing near-infrared laser energy and undergoes the photothermal transformation, and its crystal structure does not change under the action of the laser.

After studying the laser marking performance of ABS/OMMT composite materials, the effect of the laser marking process and the OMMT loading content on the mechanical properties of composite materials will be further studied. The purpose of this project is to prepare composite materials with both good laser marking performance and mechanical properties, the laser marking process has influence on the surface of the material including the change of the surface structure and hydrophobic performance. Therefore, the mechanical property tests of ABS composites before and after the laser are becoming very important. Figure 11 shows the mechanical properties of ABS/MMT, unmarked ABS/OMMT, and marked ABS/OMMT composites including tensile strength, elongation at break, and impact strength as a function of the MMT and OMMT loading content. As can be seen from Figure 11a−c, the tensile strength, fracture elongation, and impact strength of ABS are approximately 39 MPa, 22%, and 16 KJ/m², respectively. After adding the unmodified MMT, the mechanical properties of ABS decreased gradually with the increase of the MMT content. When the MMT content was 2 wt %, the tensile strength, fracture elongation, and impact strength of ABS/MMT decreased to 34 MPa, 12.5%, and 7 KJ/m². At a high content of MMT, the ABS/MMT composite becomes very brittle, and its elongation at break drops below 5%. Because the ABS/MMT has very poor mechanical performance due to the incompatibility of inorganic MMT and organic ABS chains, there is no meaning to do the laser marking work on its surface. After the addition of OMMT, the mechanical properties of the prepared ABS composite materials were significantly improved compared to the unmodified ABS/MMT. When the OMMT content was 2 wt %, the tensile strength, fracture elongation, and impact strength of the ABS/OMMT composite increased by 15, 20, and 14%, respectively, compared to ABS. This is because the modified MMT surface is full of organic groups, which greatly improved OMMT and ABS compatibility, and has a filling effect on the mechanical properties of ABS when the content is not high. However, as the OMMT content continued to increase from 2 to 8 wt %, the mechanical properties of composites are gradually decreased, indicating that there is an optimum OMMT content for achieving good mechanical properties.

Under the condition of a laser current intensity of 9 A, the tensile strength of the prepared laser-marked ABS/OMMT composite increased with the OMMT content increasing from 1 to 2 wt % and then decreased with the OMMT content further increasing to 8 wt %. The laser-marked ABS/OMMT composite with 2 wt % OMMT shows the maximum tensile strength value of 42 MPa, which is still 7.7% higher than that of ABS. The fracture elongation and impact strength of the marked ABS/OMMT composites showed a downward trend with the increase of the OMMT content. Due to the compatibility between modified MMT and ABS substrates, the mechanical properties of the marked ABS/OMMT composite are still better than those of ABS/MMT composites with the same content. Compared with the unmarked ABS/OMMT composite, the mechanical properties of the marked ABS/OMMT composite decreased, due to the influence of the laser marking process on the surface structure of the composite material. Because OMMT can absorb near-infrared laser energy and undergo photothermal reaction, the ABS chain degradation and carbonation are caused, resulting in many small cracks and holes on the surface of ABS composites, as well as irregular bumps. Note that the thickness of the specimen used for mechanical performance testing is 2 mm or 4 mm. Although the laser marking process occurs within a depth of several hundred µm on the surface of the composite material, the composite sample with this surface defect is more likely to cause damage when stretched, which still affects the mechanical properties of the composite material. According to the above analysis, the ABS composite material with 2 wt % OMMT has enhanced tensile strength, compared to ABS. When the OMMT content is higher than 2 wt %, the resulting ABS/OMMT composite material has decreased mechanical properties, which makes the surface marking of the higher OMMT content composite material lack value and significance. Therefore, in the practical application of the ABS/OMMT composites, the desirable combination of high contrast laser marking performance and mechanical properties can be achieved at an OMMT loading content of 2 wt % and a laser current intensity of 9 A. Considering that the real size or thickness of the ABS products would be much larger than the thickness dimensions of the test specimen, and the area of laser marking is much lower compared to the whole product surface, we still believe that the influence of the laser marking process will not greatly affect the mechanical performance of ABS composite materials. For example, the shell thickness of an ABS electric switch box (36 × 87 × 66 mm in length, width, and height) can reach 5 mm, which is much thicker than that of the test specimen and the penetration depth of the laser marking. Hence, there is no great influence on the mechanical properties of ABS products.

3. CONCLUSIONS

Through the organic modification of MMT and melt blending, a series of ABS/OMMT composites with different OMMT contents were prepared. The laser marking performance, surface morphology, and mechanical properties of the composites under different OMMT contents and laser marking current intensities were studied. Compared with ABS, the addition of OMMT enables the laser marking ability of ABS, and a clear and high contrast texts and patterns can be fabricated. OMMT can absorb near-infrared laser energy and undergo the photothermal conversion, so that the local overheating leads to the thermal pyrolysis and carbonization of the ABS chain, thus forming a clear laser marking. The clarity and contrast of black marks on the surface of the ABS/OMMT composite depend on the OMMT content and the laser marking current intensity. At an OMMT content of 2 wt % and marking current intensity of 9 A, the laser marking pattern has the best surface contrast (ΔE = 36.38) and clarity. SEM images and water contact angle tests indicated the presence of numerous holes and irregular bumps observed on the surface of the ABS/OMMT composite, resulting in more hydrophobic surfaces. Raman Spectroscopy and XRD confirm that amorphous carbon was formed on the composite surface after laser marking and the OMMT crystal structure has not changed. The mechanical performance tests showed that when the OMMT content is ≤2 wt %, the ABS/OMMT composite has increased properties due to the compatibility between...
OMMT and ABS. At the same OMMT content, the mechanical properties of the marked ABS/OMMT composite were lower than those of the unmarked one, due to the influence of the laser marking process on the surface properties and structure of the composite material. For the practical application of ABS/OMMT composites, the desirable combination of high contrast laser marking performance and mechanical properties can be achieved at an OMMT loading content of 2 wt % and a laser current intensity of 9 A. This research provides a simple, economical, and environmentally friendly laser-sensitive additive MMT and preparation method for large-scale application of laser-marking ABS composite materials, which is expected to be applied to the surface laser marking of other engineering materials.

4. MATERIALS AND METHODS

4.1. Chemicals and Materials. Montmorillonite (sodium montmorillonite, 50 nm, MMT) was purchased from Dongguan Mingsen Plastic Materials Co., Ltd. (Dongguan, China). Titanate coupling agents (TSL, analytical grade) come from Guangzhou Haitian Chemical Co., Ltd. Poly(acrylonitrile-co-butadiene-co-styrene) (ABS, DG-417, Melt Flow Index: 18.5 g/10 min (ASTM 1238, 220 °C, 10 Kg)) was bought from Tianjin Dagu Chemical Co., Ltd. Cetyltrimethylammonium bromide (CTAB, analytical grade) was commercially available from Shanghai Hansi Chemical Co., Ltd. 3-(trimethoxysilyl)propyl methacrylate (KH570, >98 wt %) and 3-aminopropyltriethoxysilane (KH550, >95 wt %) were purchased from Nanjing Chuangshi Chemical Auxiliary Co., Ltd. 3-aminopropyltriethoxysilane (KH550, >95 wt %) was purchased from Sinopharm Reagent, Shanghai, China. Deionized water purified with a Millipore Milli-Q system was used in all experiments.

4.2. Preparation of Organically Modified MMT. Modification of MMT with KH570, KH550, and titanate coupling agents is performed as follows. For example, typically, 54 mL of methanol and 6 mL of water were placed in a 100 mL flask and stirred well. Typically, the silane coupling agent of KH550 (2 vol %) was added, and then, the pH of the mixture was adjusted to 5.5 using acetic acid. The reaction was allowed to take place at 56 °C in an oil bath for 1.5 h. Then, 1 g of MMT was added to the above solution and stirred at 85 °C for 2 h. The product was washed with methanol, separated by filtering, and dried for 48 h at 60 °C in a vacuum oven.

Modification of MMT with a surfactant CTAB is performed as follows. MMT (1 g) was dispersed in 25 mL of water in a 100 mL round-bottom flask. CTAB aqueous solution (5 mL) (7.5 mg/mL) was slowly added drop wise to the solution above and was heated at 70 °C for 6 h. The clay was washed with ethanol and water, filtered off, and dried for 48 h at 60 °C in a vacuum oven.

4.3. Preparation of ABS/OMMT Composite Materials. ABS was previously dried for 12 h at 60 °C in order to avoid possible degradation during melt blending due to the moisture. OMMT and ABS were mixed in a torque rheometer (PPT-3/ZZL-40, Guangzhou Putong Experimental Analysis Instrument Co., Ltd.). The set temperature is 180 °C, and the blending time was 8 min, so that OMMT and ABS were fully mixed to obtain ABS/OMMT composite materials. The total mass of ABS and OMMT is 40 g, and the loading contents of OMMT are selected as 1, 2, 4, 6, and 8 wt %, respectively. The composite samples are labeled as ABS/OMMT. For example, ABS/1% OMMT indicates the incorporation of 1% of OMMT in ABS. Sheet samples of ABS/OMMT composites were obtained using a flat vulcanizing machine (XH-406B, Dongguan Zhenggong Electromechanical Equipment Technology Co., Ltd.) at a preset temperature of 180 °C.

4.4. Laser Marking Experiment. ABS/OMMT composite samples are marked with an Nd:YAG (KDD-50, Suzhou KiTe Laser Technology Co., Ltd.) pulsed laser beam at 1064 nm. The laser marking process parameters include a laser focal length of 219 mm; spot size of 100 μm; laser pulse repetition frequency of 4000 Hz; and laser scanning speed of 450 mm/s. The laser current intensity is set to 7, 8, 9, 10, and 11 A, respectively.

4.5. Instruments and Characterization. 4.5.1. X-ray Diffraction (XRD). ABS and ABS/OMMT composite materials before and after laser marking were tested on an X-ray single crystal diffractometer (APEX II DUO, Bruker). In addition, the interlayer spacing of the MMT crystal plane after organic modification was calculated using 2θ values obtained by XRD.

4.5.2. Fourier Transform Infrared Spectroscopy (FT-IR). A Nicolet iS50 infrared spectrometer (Thermo Fisher, USA) was used for the test in the range of 5000~400 cm⁻¹. The FT-IR spectra of unmodified and modified MMT were measured to prove whether the modification was successful.

4.5.3. Color Difference Analysis. An X-Rite 7000A color difference meter (X-Rite, USA) was used to test the surface of ABS/OMMT composites before and after laser marking. The color difference change (ΔE)²⁶ was used to characterize the effects of different laser-additive contents and laser intensities on the laser marking performance of ABS composites.

4.5.4. Microscope Observation. A stereo microscope (Phoenix Technology Company) was used to observe and compare the laser-marked areas of ABS composite materials. The magnification is 200 times.

4.5.5. Water Contact Angle Test. A water contact angle tester (JC2009D1 goniometer, Shanghai Zhongchen Digital Technology Equipment Co., Ltd., Shanghai, China) was employed to measure the change of the water contact angle before and after laser marking ABS composites.

4.5.6. Raman Spectroscopy. A laser confocal micro-control Raman spectrometer (DXR, Thermo Science and Technology Company) with a laser wavelength of 780 nm was used to scan the marking surface of the composite material sample. The test conditions were set as follows: a slit width of 50 μm and a laser power of 7.0 mW.

4.5.7. Scanning Electron Microscope (SEM). The surface morphology of the ABS/OMMT composite sample after laser marking was observed using a field emission scanning electron microscope (SUPRASS, Zeiss). Before observation, the sample surface was coated with gold.

4.5.8. Mechanical Property Test. The prepared ABS/OMMT composite sample was cut into a dumbbell-shaped spline with a width of 4 mm, a length of 20 mm, and a thickness of 2 mm using a CP-25 punching machine (Hebei Cangzhou Zhongya Testing Instrument Co., Ltd., China). Five complete and smooth dumbbell-shaped splines were cut out in parallel for each component sample. According to the national standard GB/T528−1998, a WDT-30 electronic universal tensile tester (Shenzhen Kaiqiangli Experimental Instrument Co., Ltd.) was used to determine the tensile strength and elongation at break. A tensile rate of 20 mm/min was used.

A WZS10G miniature injection molding machine (Shanghai Xinshuo Precision Machinery Co., Ltd.) was used to prepare specimens for impact strength tests. The specimens with a
length of 120 mm, a width of 10 mm, a thickness of 4 mm, and a width of 2 mm at the notch were obtained. A cantilever impact test (XJU-22, Chengde Precision Test Machine Co., Ltd., Chengde, China) was used for the test.

■ AUTHOR INFORMATION

Corresponding Author
Zheng Cao — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China

Yinjue Wu — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China

Yang Zhang — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China

Kailun Wang — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China

Hongxin Gao — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China

Keming Luo — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China

Junfeng Cheng — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China

Chunlin Liu — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China; Changzhou University Huaidie College, Changzhou 213016, P. R. China

Lei Zhang — Key Laboratory of Optic-electric Sensing and Analytical Chemistry for Life Science, MOE; College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, P. R. China

Juan Qi — Jiangsu Key Laboratory of Environmentally Friendly Polymeric Materials, School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovoltaic Science and Engineering, Changzhou University, Changzhou 213164, Jiangsu, P.R. China; School of Chemical Engineering, Xuzhou College of Industrial Technology, Xuzhou 221140, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02803

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project was supported by the National Natural Science Foundation of China (Grant No. 21704008) and the Applied Basic Research Project of Changzhou (Grant No. CJ20180052). Financial support provided for this project by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD) and the Top-notch Academic Programs Project of Jiangsu Higher Education Institutions (TAPP) and financial support from the Young Elite Scientist Sponsorship Program of the Jiangsu Province Association of Science and Technology and the Postgraduate Research & Practice Innovation Program of Jiangsu Province are also gratefully acknowledged.

■ REFERENCES

(1) Chen, S.; Lu, J.; Feng, J. 3D-Printable ABS Blends with Improved Scratch Resistance and Balanced Mechanical Performance. Ind. Eng. Chem. Res. 2018, 57, 3923–3931.

(2) Sreedharan, J.; Jeevanantham, A. K. Analysis of Shrinkages in ABS Injection Molding Parts for Automobile Applications. Mater. Today: Proc. 2018, 5, 12744–12749.

(3) Lay, M.; Thajudin, N. L. N.; Hamid, Z. A. A.; Rusli, A.; Abdullah, M. K.; Shuib, R. K. Comparison of physical and mechanical properties of PLA, ABS and nylon 6 fabricated using fused deposition modeling and injection molding. Composites, Part B 2019, 176, 107341.

(4) Wang, X.; Jiang, M.; Zhou, Z.; Gou, J.; Hui, D. 3D printing of polymer matrix composites: A review and prospective. Composites, Part B 2017, 110, 442–458.

(5) Donald, J. M.; Hopenhayn-Rich, C. Reproductive and development toxicity of toluene: A review. Environ. Health Perspect. 1991, 94, 237–244.

(6) Kurski, J.; Marič, B.; Adamović, D.; Mihailović, A.; Grujić, S.; Oros, I.; Krstić, J. Register of hazardous materials in printing industry as a tool for sustainable development management. Renewable Sustainable Energy Rev 2012, 16, 660–667.

(7) Odintsova, G.; Andreeva, Y.; Salmimen, A.; Roozbehani, H.; Van Cuong, L.; Yatsuk, R.; Golubeva, V.; Romanov, V.; Veiko, V. Investigation of production related impact on the optical properties of color laser marking. J. Mater. Process. Technol. 2019, 274, 116263.

(8) Shuvakoti, I.; Kibria, G.; Pradhan, B. Predictive model and parametric analysis of laser marking process on gallium nitride material using diode pumped Nd:YAG laser. Opt. Laser Technol. 2019, 115, 58–70.

(9) Kučera, M.; Martan, J.; Fran, A. Time-resolved temperature measurement during laser marking of stainless steel. Int. J. Heat Mass Transfer 2018, 125, 1061–1068.
Enhanced laser marking of polypropylene induced by core-shell ATO@IPI laser-sensitive composite. Polym. Degrad. Stab. 2019, 167, 77–85.

(20) Feng, J.; Zhang, J.; Zheng, Z.; Zhou, T. New Strategy to Achieve Laser Direct Writing of Polymers: Fabrication of the Color-Changing Microcapsule with a Core–Shell Structure. ACS Appl. Mater. Interfaces 2019, 11, 41688–41700.

(21) Wen, L.; Zhou, T.; Zhang, J.; Zhang, A. Local Controllable Laser Patternning of Polymers Induced by Graphene Material. ACS Appl. Mater. Interfaces 2016, 8, 28077–28085.

(22) Jia, L.; Zhang, J.; Su, G.; Zheng, Z.; Zhou, T. Locally Controllable Surface Foaming of Polymers Induced by Graphene via Near-Infrared Pulsed Laser. ACS Sustainable Chem. Eng. 2020, 8, 2498–2511.

(23) Cheng, J.; Li, H.; Zhou, J.; Cao, Z.; Wu, D.; Liu, C. Influence of diamantino trioxide on laser-marking properties of thermoplastic polylethylene. Polym. Degrad. Stab. 2018, 154, 149–156.

(24) Cao, Z.; Chen, Y.; Zhang, C.; Cheng, J.; Wu, D.; Ma, W.; Liu, C.; Pu, Z. Preparation of near-infrared laser responsive hydrogels with enhanced laser marking performance. Soft Matter 2019, 15, 2980–2995.

(25) Cao, Z.; Hu, Y.; Lu, Y.; Xiong, Y.; Zhou, A.; Zhang, C.; Wu, D.; Liu, C. Laser-induced blackening on surfaces of thermoplastic polyurethane/BiOCl composites. Polym. Degrad. Stab. 2017, 141, 33–40.

(26) Zhang, C.; Dai, Y.; Lu, G.; Cao, Z.; Cheng, J.; Wang, K.; Wen, X.; Ma, W.; Wu, D.; Liu, C. Facile Fabrication of High-Contrast and Light-Colored Marking on Dark Thermoplastic Polyurethane Materials. ACS Omega 2019, 4, 20787–20796.

(27) Zhou, J.; Cheng, J.; Zhang, C.; Wu, D.; Liu, C.; Cao, Z. Controllable Black or White laser patterning of polypropylene induced by carbon nanotubes. Mater. Today Commun. 2020, 24, 100787.

(28) Yang, H.; Yu, B.; Song, P.; Maluk, C.; Wang, H. Surface-coating engineering for flame retardant flexible polyurethane foams: A critical review. Composites, Part B 2019, 176, 101785.

(29) Cao, Z.; Lu, Y.; Zhang, C.; Zhang, Q.; Zhou, A.; Hu, Y.; Wu, D.; Tao, G.; Gong, F.; Ma, W.; Liu, C. Effects of the chain-extender content on the structure and performance of poly(lactic acid)–poly(butylene succinate)–microcrystalline cellulose composites. J. Appl. Polym. Sci. 2017, 134, 44895.

(30) Xia, Y.; Tang, R.; Tao, S.; Tao, G.; Gong, F.; Liu, C.; Cao, Z. Epoxy resin/phosphorus-based microcapsules: Their synergistic effect on flame retardation properties of high-density polyethylene/graphene nanoplatelets composites. J. Appl. Polym. Sci. 2018, 135, 46662.

(31) Yeoile, P.; Ning, H.; Hassen, A. A.; Vaidya, U. K. The Effect of Flocculent, Dispersants, and Binder on Wet—laid Process for Recycled Glass Fiber/PA6 Composite. Polym. Compos. 2018, 26, 259–269.

(32) Tang, L.; He, M.; Na, X.; Guan, X.; Zhang, R.; Zhang, J.; Gu, J. Functionalized glass fibers cloth/spherical BN fillers/epoxy laminated composites with excellent thermal conductivities and electrical insulation properties. Compos. Commun. 2019, 16, 5–10.

(33) Teimouri, A.; Ghanavati Nasab, S.; Habibollahi, S.; Fazel-Najafabadi, M.; Chermahini, A. N. Synthesis and characterization of a chitosan/montmorillonite/ZrO2 nanocomposite and its application as an adsorbent for removal of fluoride. RSC Adv. 2015, 5, 6771–6781.

(34) Chen, D.; Li, W.; Wu, Y.; Zhu, Q.; Lu, Z.; Du, G. Preparation and characterization of chitosan/montmorillonite magnetic microspheres and its application for the removal of Cr (VI). Chem. Eng. J. 2013, 221, 8–15.

(35) Gao, D.; Li, R.; Lv, B.; Ma, J.; Tian, F.; Zhang, J. Flammability, thermal and physical-mechanical properties of cationic polymer/ montmorillonite composite on cotton fabric. Composites, Part B 2015, 77, 329–337.

(36) El Haouti, R.; Ouachtak, H.; El Guerdouani, A.; Amédieu, A.; Amater, E.; Haounati, R.; Addi, A. A.; Akbal, F.; El Alem, N.; Taha, M. L. Cationic dyes adsorption by Na-Montmorillonite Nano Clay: Experimental study combined with a theoretical investigation using DFT-based descriptors and molecular dynamics simulations. J. Mol. Liq. 2019, 290, 111139.

(37) Zhang, D.; Williams, B. L.; Shrestha, S. B.; Nasir, Z.; Becher, E. M.; Lofink, B. J.; Santos, V. H.; Patel, H.; Peng, X.; Sun, L. Flame retardant and hydrophobic coatings on cotton fabrics via sol-gel and self-assembly techniques. J. Colloid Interface Sci. 2017, 505, 892–899.

(38) Li, Y.; Schulz, J.; Mannen, S.; Delhom, C.; Condon, B.; Chang, S.; Zammarno, M.; Grunlan, J. C. Flame Retardant Behavior of Polyelectrolyte—Clay Thin Film Assemblies on Cotton Fabric. ACS Nano 2010, 4, 3325–3337.

(39) Triantafyllidis, K. S.; LeBaron, P. C.; Park, I.; Pinnaavaia, T. J. Epox–Clay Fabric Film Composites with Unprecedented Oxygen-Barrier Properties. Chem. Mater. 2006, 18, 4393–4398.

(40) Jesus, C. R. N.; Molina, E. F.; Pulcinelli, S. H.; Santillí, C. V. Highly Controlled Diffusion Drug Release from Ureasil–Poly(ethylen oxide)−Na+–Montmorillonite Hybrid Hydrogel Nano-composites. ACS Appl. Mater. Interfaces 2018, 10, 19059–19068.

(41) Kouser, R.; Vashist, A.; Zafaryab, M.; Rizvi, M. A.; Ahmad, S. Na-Montmorillonite-Dispersed Sustainable Polymer Nanocomposite Hydrogel Films for Anticancer Drug Delivery. ACS Omega 2018, 3, 15809–15820.

(42) Duchek, P.; Urbanová, M.; Pokorná, D.; Kupčík, J.; Šubrt, J.; Pola, J. Laser-induced ablative amorphization of montmorillonite. J. Non-Cryst. Solids 2012, 358, 3382–3387.

(43) Yeole, P.; Ning, H.; Hassen, A. A.; Vaidya, U. K. The Effect of Flocculent, Dispersants, and Binder on Wet—laid Process for Recycled Glass Fiber/PA6 Composite. Polym. Compos. 2018, 26, 259–269.

(44) Greesh, N.; Sanderson, R.; Hartmann, P. C. Functionalization of montmorillonite by end-chain mono-cationic polystyrene and end-
chain mono-cationic poly(styrene-b-2-hydroxethyl acrylate). Appl. Clay Sci. **2014**, *93-94*, 38–47.

47) Shen, W.; He, H.; Zhu, J.; Yuan, P.; Frost, R. L. Grafting of montmorillonite with different functional silanes via two different reaction systems. *J. Colloid Interface Sci.* **2007**, *313*, 268–273.

48) Pourabas, B.; Raeisi, V. Preparation of ABS/montmorillonite nanocomposite using a solvent/non-solvent method. *Polymer* **2005**, *46*, 5533–5540.

49) Li, J.; Zhou, Y.; Fan, F.; Du, F.; Yu, H. Controlling surface wettability and adhesive properties by laser marking approach. *Opt. Laser Technol.* **2019**, *115*, 160–165.

50) Ferrari, A.; Robertson, J. Resonant Raman spectroscopy of disordered, amorphous, and diamondlike carbon. *Phys. Rev. B* **2001**, *64*, No. 075414.

51) Liu, C.; Lu, Y.; Xiong, Y.; Zhang, Q.; Shi, A.; Wu, D.; Liang, H.; Chen, Y.; Liu, G.; Cao, Z. Recognition of laser-marked quick response codes on polypropylene surfaces. *Polym. Degrad. Stab.* **2018**, *147*, 115–122.