Identification of the zinc dispersion in rubber blends by libs with a Nd:YAG laser

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Abstract：Laser-induced breakdown spectroscopy（LIBS） is a laser based method for the qualitative and quantitative analysis of chemical elements. It could be used for the analysis of rubber blends in the mixing room. In this paper, zinc dispersion in rubber blends is detected with LIBS by using a Nd:YAG laser with a wavelength of 1 064 nm and a pulse energy of 100 mJ. Experiments show that the quality of rubber products depends on the correct blending of the mixing components. For example short mixing times can lead to an inhomogeneous dispersion of these components. The intensity of the spectral lines is strongly affected by the setup parameters like the focal position. The use of calibration samples allows creating a calibration curve. Based on line scans, the zinc dispersion in these rubber blends can be analyzed. Variations in the homogeneity of the zinc caused by short mixing times or different rotation speed of the mixer can be detected by the evaluation of the intensity profile along these line scans.

Key words：LIBS；rubber；Nd:YAG-Laser；zinc

利用 Nd:YAG 激光诱导击穿光谱法
检测橡胶共混物中锌的均匀性分布

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摘要：激光诱导击穿光谱是一种基于激光的定性、定量分析化学元素的方法，可用于分析混合室中的橡胶共混物。本文采用波长为 1 064 nm、脉冲能量为 100 mJ 的 Nd:YAG 激光诱导击穿光谱法检测橡胶共混物中锌的分散情况。实验表明，正确混料决定了橡胶产品的质量，较短的混合时间将会导致混料的不均匀分散；焦距等参数设置对光谱线强度影响较大。激发标定样品可产生标定曲线。通过行扫描可分析锌在橡胶共混物中的分散情况。通过估算沿着行扫描方向的强度分布，可检测由于混合时间较短和旋转速度不同而引起的锌均匀性变化。

关　　键　　词：激光诱导击穿光谱；橡胶；Nd:YAG 激光器；锌

1   Introduction

Scarce resources and increasing requirements to compete with each other internationally make it necessary to integrate new systems in modern production processes and to be more efficient. An essential area is quality management. Quality management systems have to be usable in offline and online application. One major intention is to reduce the amount of scrap from manufacturing materials.

Quality management is also an essential issue in the rubber industry. Rubber has many applications including tires, pipes, conveyor belts and many more parts. Experience shows that an irregular dispersion of the blending components can lead to a suboptimal rubber article. One such component is zinc oxide. Zinc oxide leads to better heat conductivity and reinforcement in tires[1]. The rubber industry also uses zinc oxide as a ultraviolet(UV) stabilizer[1].

The number of rotor revolutions of the mixer has a huge influence on the dispersion of the blending components[2]. By improving the mixing technique it is possible to improve the dispersion of the blending components. While the process is improving the irregular dispersion of the blending components it is still a significantly topic. Furthermore the evaluation of the homogeneous dispersion of the blending components is very challenging. Because current quality management methods, such as Mooney viscosity and stretching tests, do not provide direct information about the dispersion of the blending components, it is important to provide a practical method which allows the evaluation of the dispersion of the blending components.

In Ref.［3］a laser induced emission spectral analysis is shown, which is applicable as an instrument for quality assurance of rubber blends. Based on multiple measurements at different locations on the sample, it is possible to evaluate the dispersion

in the sample. An excimer laser with 248 nm and maximum 1 000 mJ pulse energy was used. The measurements were realized with shielding gas. The analyzed wavelength is in the range of 170 − 480 nm. The major disadvantage of this method is the huge size of the laser and the required vacuum for the spectroscope which makes it an inflexible tool. In fact it is not applicable for industrial application.

2   LIBS

Laser-induced breakdown spectroscopy(LIBS) is a laser based method for the qualitative and quantitative analysis of chemical elements. LIBS can be applied to solid, liquid and gas samples, which makes it a very flexible tool. The major advantage of LIBS is without sample preparation. LIBS is a very fast analysis method so it is able for offline and online application. The laser beam is focused on the sample surface to generate a plasma. The plasma emits radiation which is analyzed by a spectroscope. Based on the focus size and the laser energy, only a small amount of the sample surface is destroyed. More details are shown in Ref.［4-5］.

Because of the advantages, LIBS becomes an important tool for industrial applications. In addition to its function as a normal analysis tool, LIBS can also be used for recycling or characterization applications. One of application fields is the recycling of plastic where high process speed and the possibility of online and non-destructive analysis are required[6]. Another application field is the identification of steel[7-9]. In this field LIBS can be used to ensure material composition.

3   Experimental Setup

The rubber samples which have been used for the experiments were provided by the DIK(Deutsches Institut für Kautschuktechnologie e. V.).

The experimental setup is shown in Fig. 1. The

sample chamber, the LIBS-head and the spectroscope console are from Applied Photonics Ltd. As a laser source, a Nd: YAG laser with a wavelength of 1 064 nm, maximum 100 mJ pulse energy, 8 ns pulse duration and a repetition rate of 1 – 20 Hz was used. The experiments were operated with the maximum pulse energy of 100 mJ and a repetition rate of 10 Hz.
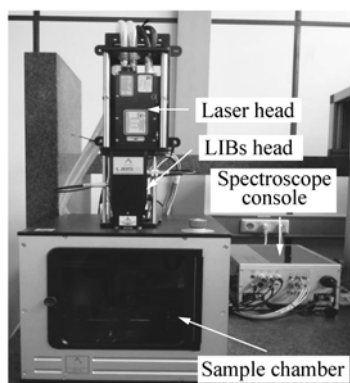

Fig. 1 Sample chamber with LIBS-head, laser-head and spectroscope console

The sample chamber ensures the laser security and also includes a computer based translation stage which allows scanning of the sample surface. The spectroscope console contains 5 spectroscopes. Each spectroscope provides a specific wavelength range. Tab. 1 gives an overview about the spectroscope specifications.

Tab. 1 Spectroscope specification

Spectroscope	Wavelength/nm	Grating	Resolution/nm
1	314 – 416	3 600	0. 06
2	414 – 498	2 400	0. 09
3	496 – 718	1 200	0. 18
4	716 – 904	1 200	0. 18
5	804 – 977	1 200	0. 18

The spectroscopes provide a wavelength range of 314 – 977 nm. The setup was chosen because of its advantages concerning industrial requirements. The small and robust construction of the setup allows a high mobility. The use of a compact laser system

makes the setup cost efficient.

The schematic setup of the LIBS-head is shown in Fig. 2. The laser beam is focused on the sample surface to generate a plasma. Focal length is 80 mm. Theoretical minimum spot size is approx. 25 μm. By moving the beam expander it is possible to position the focal beam on the sample. The emitted radiation is guided to the spectroscopes (see Tab. 1) by lenses and optical fibers. The aperture nozzle ensures that the sample surface and the plasma are effectively purged with argon. The argon has two functions. Firstly the argon stream protects the lenses against pollution which accrues by the plasma generation. Secondly the argon influences the properties and the dynamics of the plasma which leads to higher signal intensity[10]. The aperture nozzle also acts as a reference level for the sample positioning.
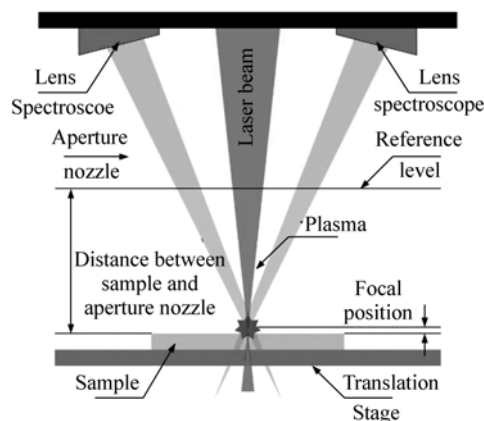

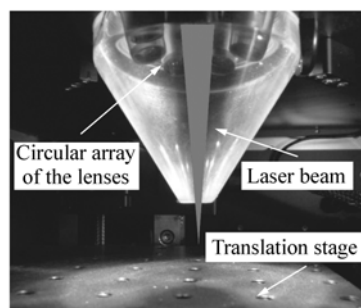Fig. 2 Schematic setup of the LIBS-head and the focal position of the laser beam and the spectroscopes

Fig. 3 View into the sample chamber and the optical elements

Fig. 3 shows the view into the sample chamber. The red and blue tubes are the holders for the lenses. The laser beam expands in the middle of these tubes.

4　Experimental Results

The goal of investigation was to check the possibility to detect the zinc dispersion in rubber blends with LIBS with a Nd: YAG laser. Information about relevant zinc spectral lines are listed in spectra databases [11] and [12]. The NIST-Database indicates Zn(Ⅰ) lines with a high intensity at 213.9 nm, 280.1 nm, 328.2 nm, 330.3 nm, 334.5 nm, 468.0 nm, 472.2 nm, 481.1 nm and 636.2 nm[11].

In the first step it was necessary to find out the best setup parameters for the experiments. As shown in Fig. 2, it is possible to change the distance between the sample surface and the aperture nozzle by lifting or lowering the sample. This leads to a shift of the plasma in the focal position of the spectroscopes. If the distance between the sample surface and the aperture nozzle is too small or too big, the generated plasma is out of the field of vision of the spectroscopes. Furthermore it is possible to change the focal position of the laser beam on the sample surface by moving the beam expander which leads to different surface intensities. In fact, the intensity of the zinc spectral lines depends on these two parameters. Fig. 4 shows the mean zinc intensity of aluminium alloy calibration sample at 481.1 nm as a function of these two parameters. The aluminium alloy calibration sample contains 7.36% zinc and was used to ensure a homogeneous zinc dispersion. The measurement raster was measured with a step size of 0.5 mm. For the calculation of the mean zinc intensity, 10 spectra were taken at each measurement point. The intensity between two measurement points was interpolated linear. The different colours indicate the zinc intensity. Red and blue indicate the

highest and the lowest zinc intensity, respectively. For the further experiments the parameter from the red marked area were taken. The focal position of the laser beam was fixed with -3 mm in the sample and the distance between the aperture nozzle and the sample surface was fixed with 5 mm.
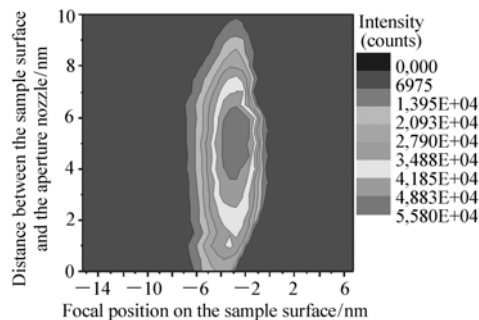

Fig. 4　Zinc intensity of an aluminium alloy calibration sample at 481.1 nm depending on the focal position of the laser beam and the distance between the aperture nozzle and the sample surface

In the next step a reference spectra were taken from a sample which only contains natural rubber and a sample which contains natural rubber and 10 phr(per hundred rubber) zinc oxide to locate the relevant zinc lines for this sample composition. The reference spectra are shown in Fig. 5.
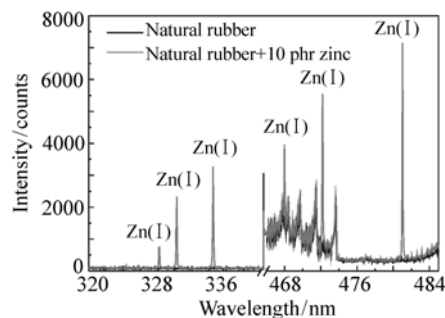

Fig. 5　Reference spectra of natural rubber and natural rubber + 10 phr zinc

The spectrum of the rubber zinc sample (red marked curve) shows the characteristic zinc lines at 328.2 nm, 330.3 nm, 334.5 nm, 468.0 nm, 472.2 nm and 481.1 nm. These lines agree with the information form the NIST-Database[11]. These lines

do not occur in the reference spectrum of the rubber sample(black marked curve). The highest intensity provides the spectral line at 481. 1 nm which makes it practical for the further investigations.

To get an information about the zinc concentration in rubber samples, it is necessary to create a calibration curve. The result from this experiment is shown in Fig. 6. The points in the chart show the mean zinc intensity at 481. 1 nm for rubber samples which contain 0. 5, 1. 0, 1. 5, 5. 0, 10. 0 and 20. 0 phr zinc. The mean zinc intensity of each sample was determined based on 10 measuring points per sample. At each measuring point 20 spectra were taken. To avoid the influence of a polluted surface, 5 cleaning shots were carried out at each measuring point to clean the sample surface. The error bar shows the standard deviation. The line shows the linear gradient between the zinc intensity at 481. 1 nm and the zinc concentration in the rubber sample.
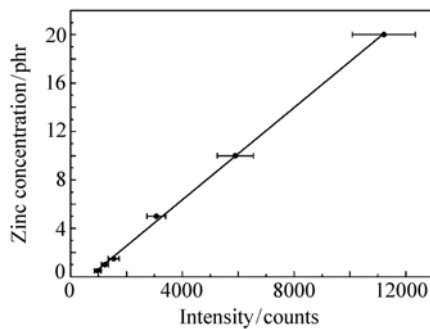

Fig. 6　Zinc concentration as a function of the signal intensity at 481. 1 nm

A difficult challenge in the manufacturing of rubber products is the homogeneous dispersion of the blending components. Fig. 7 shows an energy dispersive X-ray scanning of two rubber blends. These samples contain 4 phr zinc. Fig. 7(a) shows the zinc dispersion of sample A which was mixed with 40 revolutions per minute and Fig. 7(b) shows the zinc dispersion of sample B which was mixed with 70 revolutions per minute. Each mixing process has the same mixing time. Sample A shows agglomerations

of zinc(white spots which are encircled) which indicates an inhomogeneous zinc dispersion. Comparisons to Sample B there are no observable zinc agglomeration which indicates a homogeneous zinc dispersion. Higher revolutions per minute at the same mixing time lead to a homogeneous zinc dispersion in the rubber blend.
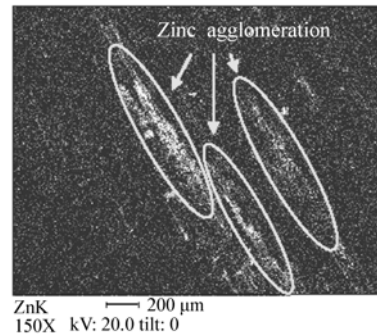
(a) Sample A mixed with 40 revolutions per minute
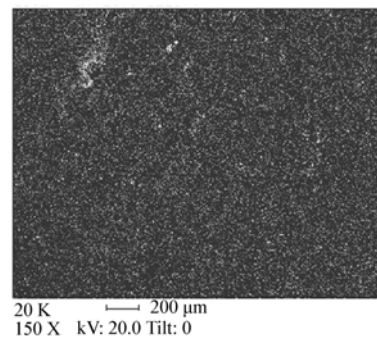
(b) Sample B mixed with 70 revolutions per minute

Fig. 7　Energy dispersive x-ray scanning of the zinc dispersion in the rubber sample(figure adaption: lightness = +20% and contrast = +20%)

To get an information about the zinc dispersion based on LIBS, it is necessary to operate regional measurements. Therefore, 5 line scans on different positions of the sample surface were carried out. Each line scan comprised 20 measuring points with an interval of 0. 5 mm. 10 spectra were accumulated at each measuring point. For the evaluation of the zinc dispersion the knowledge about the variation coefficient is important. This value represents the variance of the zinc intensity along the line scan. Zinc agglomerations which cross a line scan lead to a regional increase of the zinc intensity. The variation

coefficient attends as a dimension for the zinc dispersion. If the variation coefficient is high, the zinc dispersion is inhomogeneous. If the variation coefficient is low, the zinc dispersion is homogeneous.

Tab. 2 shows the variation coefficient of the line scans for the sample A and the sample B. Sample A

Tab. 2　Variation coefficient of the zinc intensity at 481. 1 nm of different line scans for a mixing process with 40（sample A）and 70（sample B）revolutions per minute

Line scan	Variation coefficient/%	
	sample A	sample B
1	31. 8	7. 8
2	37. 0	7. 8
3	26. 3	12. 6
4	29. 4	7. 4
5	30. 4	6. 7

shows a variation coefficient of 26. 3% up to 37. 0%. Sample B shows a much lower variation coefficient of 6. 7% up to 12. 6%. The lower variation

coefficient indicates a homogenous zinc dispersion. This result agrees with the result from the energy dispersive X-ray scanning in Fig. 7.

5　Conclusion and Outlook

It is possible to detect zinc in rubber blends by using LIBS with a Nd：YAG laser. The intensity of the zinc spectral lines depends on the correct focal position of the laser beam and the spectroscopes. The determined calibration line shows a linear relation between the intensity of the zinc spectral line at 481. 1 nm and the zinc concentration in the rubber sample. The analysis of the variation coefficient provides the evaluation of the zinc dispersion in a rubber sample. The chosen setup is mobile, robust and cost efficient, which makes it very interesting for industrial applications. The results provide opportunity for further research into LIBS online measurements for rubber production process.

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