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Potentialities of a Laser-Induced Breakdown Spectroscopy Technique in the Study of Polymer Composites

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Abstract

A laser-induced breakdown spectroscopy (LIBS) technique was used to evaluate the filler content in particulate epoxy–copper composites. A potential application for a direct and fast measurement of the filler in composites through the LIBS results is suggested using calibrated samples. The methodology used in this work makes possible the incorporation of LIBS as a quantitative technique for the study of particle metal-filled epoxy composites, providing a method to obtain a direct estimation of the filler volume fraction.

Keywords

Laser-induced breakdown spectroscopy, LIBS, epoxy composites, copper, plasma

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Introduction

Polymers generally exhibit a low elastic modulus and strength with respect to other materials such as metals or ceramics. In order to improve their mechanical properties, polymers are reinforced with inclusions (fibers, whiskers, platelets, or particles), and the final material, that is, the composite, has better properties compared to those achieved in the matrix.[1] Polymer matrix composites are commonly used in many industrial applications. Such composites are widely used because of their unique attributes, such as easy production, light weight, and generally a ductile nature. However, there are specific problems that need to be resolved in order to develop a complete understanding and to model the composite, with the aim of predicting their properties and the response of the material in service. Some of the issues that have been studied are, for example, the formation of an interphase region,[2] the influence of the filler on the curing for thermoset matrix[3] and the effect of the particle size on the physical properties of the composite,[4] among others. Within the area of the present research, some of the authors developed a specific evaluation of the content of filler particles in copper matrix epoxy composites by means of positron annihilation lifetime spectroscopy.[5]

Specifically, the content of filler is an important parameter in order to evaluate the response of the final material. For example, it can be mentioned that the elastic properties are a function of the filler content, as has been studied in several types of composites from decades ago. In particular, the elastic modulus increases significantly as a function of the content of copper particles in an epoxy matrix.[6] In addition, the electrical and thermal properties are strongly influenced by the inclusion of filler, as was reported by Boudenne et al. in polypropylene matrix composites with copper particles.[4] In both cases mentioned, the fraction of filler is the main parameter that defines the physical properties of the entire material. In general, the filler is expected to be distributed homogeneously in the sample, but the viscosity of the mixture prevents a good blending. Therefore, in parts with complex shapes, there may be regions with lower or higher filler content with respect to the nominal value. As a consequence,

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it is important to obtain the distribution of the filler content with accuracy, but in a nondestructive, fast, and inexpensive way.

Laser-induced breakdown spectroscopy (LIBS) is a technique that analyzes the radiation emitted by a laser-induced plasma. This technique allows the determination of atomic and ionic lines and then the composition of gases, liquids, or solids around the plasma. LIBS was first reported in 1962 and has evolved over the years.[7,8] Since the middle of the 1980s, renewed interest has emerged as a consequence of the development of more robust lasers of small size and low cost. LIBS is a technique that provides an accurate in situ quantitative chemical analysis. Thanks to the advances made in the new spectral processing algorithms in the last decade, improved performance has been developed, specifically in quantitative chemical analysis at atomic level.[9] The application field of LIBS has been greatly expanded due to the above-mentioned performance improvements, minimal sample preparation requirements, and LIBS being minimally destructive.[10,11] Specifically, LIBS has proven to be useful in different areas: identification of polymers[12,13] and post-consumer plastics,[14] metals[15] and detection of contaminants in algae.[16] However, to our knowledge, there is a scarce bibliography on the use of LIBS in polymeric matrix composites.[17] Moreover, the formation of plasma in materials composed of two or more well differentiated phases (epoxy/metal, for example) has been little studied. It is worth mentioning that the elasticity, thermal conduction, and surface properties have a strong influence on plasma generation and those characteristics are quite different between epoxy and metal.

In this work, taking advantage of the possibilities of the LIBS technique allowed for the determination of the content of metal filler (*Cu*) in epoxy matrix composites from LIBS measurements. The composites were prepared using different filler volume fractions with particles of copper with a size of 75 μm. This study seeks to enhance the capabilities of the technique through its use in a specific problem in the field of material science.

Materials and Methods

The studied composites were prepared using a system diglycidyl ether of bisphenol A (DGEBA) cured with an anhydride (MTHPA) and an accelerator (tertiary amine) (DGEBA, MTHPA and tertiary amine were provided by Huntsman). The DGEBA (100 parts by weight (pbw)) and MTHPA (90 pbw) were mixed and stirred at room temperature in vacuum for 30 min. Then, the accelerator (0.7 pbw) was added and the mixture was stirred again for 5 min under vacuum. Finally, an appropriate amount of filler particles was incorporated, and the mixture was stirred under vacuum until a good dispersion of the particles in the resin was achieved. The compound was poured into a Pyrex tubular mold and held horizontally in a tubular oven. In the curing process, the mixture was heated to 393 K at a rate of 0.8 K/min, and at the end of the heating process, the samples were kept at a constant temperature (393 K) for 14 h. The composites were prepared using *Cu* powder with particle diameters close to 75 μm for *Cu*. The filler volume fraction was between 5% and 30% and is considered as a nominal value.

The LIBS measurements were carried out using a neodymium-doped yttrium aluminum garnet (Nd:YAG) Q-switched pulsed laser system, Model Ultra, developed by Big Sky Laser Technologies Inc. The wavelength was 1064 nm, with a pulse duration of 5–7 ns full width half-maximum, energy of 50 mJ/pulse, and repetition rate of 2 Hz, to generate the plasmas in air at atmospheric pressure on the samples. The laser beam was focused normal to the surface of the samples, with an anti-reflective coating lens and a focal length of 200 mm. The samples were placed on a platform and were continuously rotated in order to prevent the formation of a deep crater. The spatially integrated emission of the laser-induced plasmas was collected along the line-of-sight in a direction perpendicular to the laser beam. For this, a fused silica quartz lens with a focal length of 100 mm was used, focusing on the inlet slot (100 μm wide) of a Model 504 monochromator provided by Acton Research Corporation, with an optical path length of 0.5 m, a grid of 1200 lines/mm, and a spectral range of 200–1000 nm. The detector was a non-intensified arrangement of PDA photodiodes without temporal discrimination and covering spectrum regions of 50 nm, Model RY-1024, provided by Princeton Instruments Inc.

The detection starts with each shot by a trigger signal of the laser. The radiation emitted in each shot was integrated throughout the duration of the plasma. The data acquisition and the configuration of the parameters of the experiment (for example, exposure time) was performed using a personal computer.

Craters of approximately 1 mm diameter were observed in the composite samples. In each sample, an exposure time of 20 s was used, and three sets of measurements were made. In total, 100 shots were done in each sample. In this experimental setup, the laser and plasma emission were transmitted at atmospheric pressure.

Results and Discussion

In Fig. 1, micrographs of the crater edges produced by laser shots are shown. The lighter regions are the copper particles within the composite, while the darker regions are particles detached during polishing. In each shot, an area containing many copper particles is irradiated.

The LIBS spectra of the composites containing 5%, 10%, 20%, and 30% of copper volume fraction (f_{Cu}), recorded in the spectral range of 440 nm to 540 nm are shown in Fig. 2. A smoothing ($n = 5$) was applied to the raw spectra. *Cu* lines at 510.5 nm, 515.3 nm, 521.8 nm, and 529.2 nm were identified.

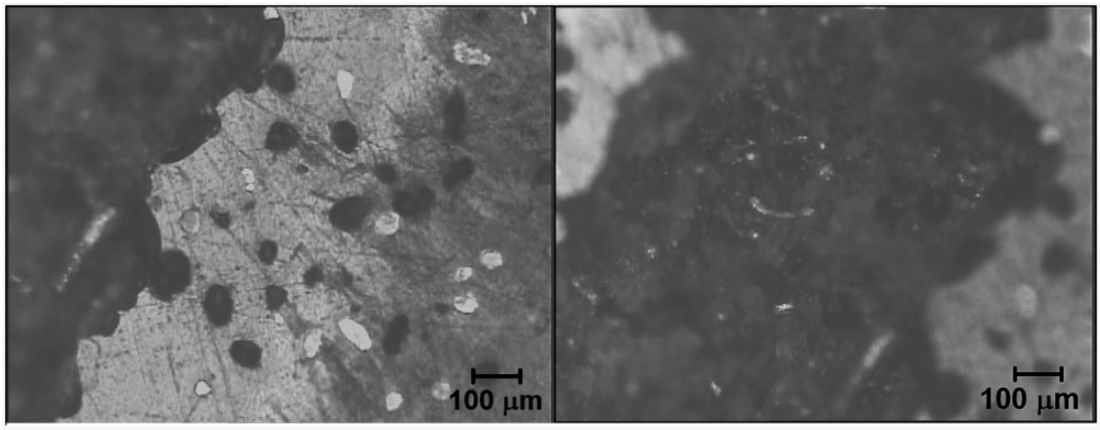

Figure 1. Micrographs of composites in the zones where the laser induced the plasma.

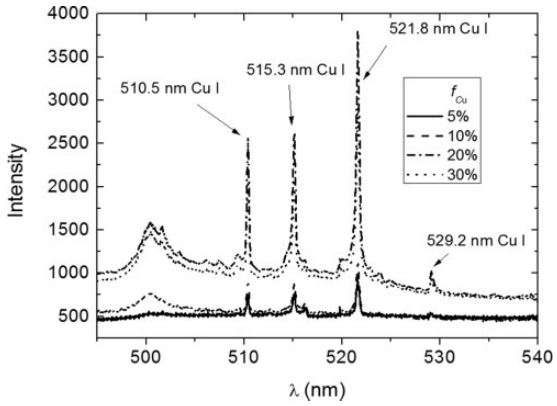

Figure 2. LIBS spectra of the studied composites with different f_{Cu}. The characteristic *Cu* lines are identified.

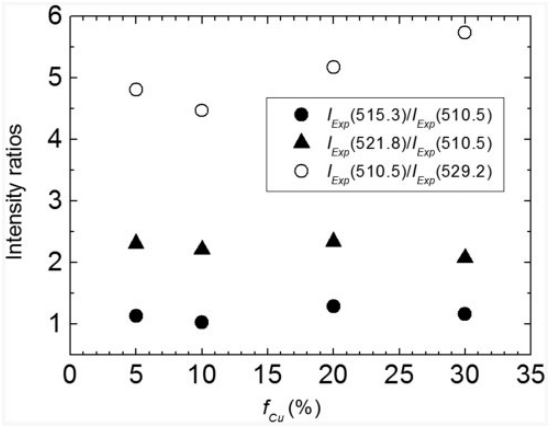

Figure 4. Intensity ratios between different lines.

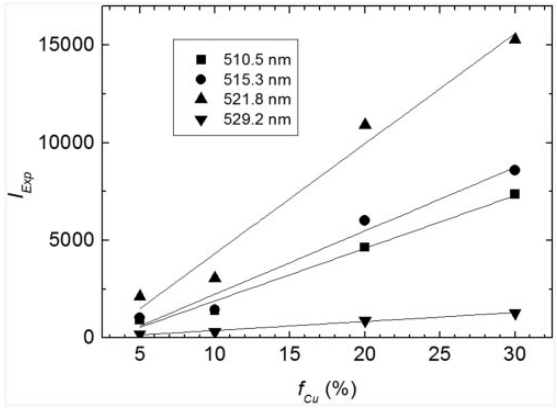

Figure 3. Intensity of peaks at 510.5 nm, 515.3 nm, 521.8 nm, and 529.2 nm as a function of f_{Cu}. Each line corresponds to a linear fit of the experimental results.

The peaks were fitted using a Lorentz function, and the area of each peak was obtained from the fit. The values of the areas (I_{Exp}) are presented in Fig. 3 as a function of f_{Cu}. In general, a linear behavior is observed for all lines.

In Fig. 4, the ratios between the intensities I_{Exp} of different lines are shown. Three representative combinations of lines were chosen: I_{Exp} (521.8 nm)/I_{Exp} (510.5 nm); I_{Exp} (515.3 nm)/I_{Exp} (510.5 nm) and I_{Exp} (510.5 nm)/I_{Exp} (529.2 nm). For all the ratios, the values are similar for different f_{Cu}, and the higher deviation is obtained for the ratio I_{Exp} (515.3 nm)/I_{Exp} (510.5 nm) in the sample with f_{Cu} of 5%. Considering this deviation within the tolerance range of the values obtained for different f_{Cu}, a low self-absorption could be expected.

The aim of this work is to perform a procedure that allows estimating the proportion of copper particles in the composites from the LIBS measurements in an easy, inexpensive, and nondestructive way. In this sense, the intensity

Table I. Parameters of the linear fits of peak intensity as a function of filler content and vice versa (see Figs. 3 and 5).

	I_{Exp} as a linear function of f_{Cu} (%)			f_{Cu} (%) as a linear function of I_{Exp}		
Peak (nm)	Intercept	Slope	*R*-square	Intercept	Slope	*R*-square
510.5	810 (±440)	270 (±23)	0.978	3.4 (±1.4)	3.7 (±0.3) 10^{-3}	0.978
515.3	1019 (±736)	325 (±39)	0.958	3.5 (±1.9)	3.0 (±0.4) 10^{-3}	0.958
521.8	−1317 (±1190)	564 (±63)	0.963	2.7 (±1.9)	1.7 (±0.2) 10^{-3}	0.963
529.2	−75 (±70)	46 (±4)	0.981	1.8 (±1.4)	2.1 (±0.2) 10^{-2}	0.981

of each line will be analyzed as a function of the copper volume fraction. Following the behavior of both parameters experimentally obtained in Fig. 3, a fit was done using a linear function of the I_{Exp} as a function of f_{Cu}. The results of the fit are presented in Table I. A good fit was observed in all cases (*R*-square of 0.958 in the worst case), then a linear relation between filler content and copper lines intensity will be assumed.

In order to have a procedure to analyze unknown samples, as a first step, the limit of detection (LOD) was determined. LOD is a parameter that is generally reported and this is defined as the lowest concentration of an analyte that can be detected with a predetermined confidence level.[18] In LIBS measurements, LOD is calculated from the slope of the linear regression (Fig. 3) and the standard deviation of the background σ as follows[18]

$$\mathrm{LOD} = \frac{3\sigma}{slope} \tag{1}$$

From measurements of filled copper composites presented in this work, LOD was between 0.9% in the worst case (529.2 nm line) and 0.07% in the best case (521.8 nm line). However, these values of LOD do not represent the detection limit associated to an experiment, because there are other factors that could increase it. If the number of particles decreases, there is a lower probability of being ablated in a laser shot. Then, more laser shots should be used in each LIBS measurement. As a first approximation, considering the spherical particles distributed homogenously in a 5% (vol) filled sample, a volume of $3.5 \times 10^7\,\mu m^3$ is necessary to find a particle. Considering that the area of the laser shot is circular with a radius of 250 μm and an ablation depth of 100 μm, then $\sim 2 \times 10^7\,\mu m^3$ of material would be removed in each shot. From a first approximation, 1.8 shots are needed to find a particle, on average. In this study, 100 shots were performed in each sample, then approximately 55 particles were ablated. Noting that this number of particles allowed to obtain an acceptable spectrum, if a sample with lower filler content is measured, a larger number of shots will be necessary. For example, for 1% of filler content, around 500 shots will be necessary.

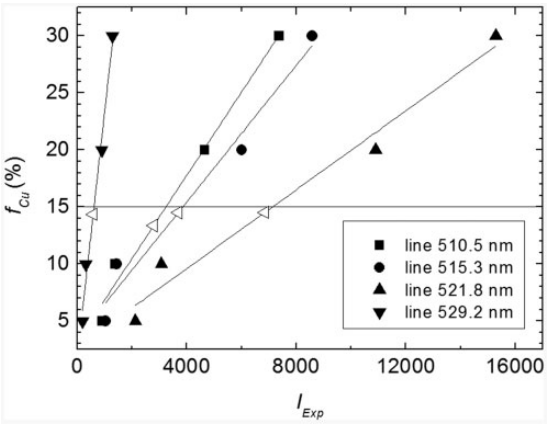

Figure 5. With each line corresponding to a linear fit of the experimental results, f_{Cu} is a function of the intensity of the peaks at 510.5 nm, 515.3 nm, 521.8 nm, and 529.2 nm. The open symbols correspond to a sample containing 15% of copper particles, used as the unknown sample.

As was mentioned above, LOD depends on the slope of the I_{Exp} versus f_{Cu} curve. However, the error of the slope is not considered in the calculation of this parameter.

On the other hand, to achieve a procedure for determining the filler content in composites, a plot of f_{Cu} as a function of I_{Exp} is more useful. In Fig. 5, f_{Cu} as a function of I_{Exp} is shown, and the linear fits made for each line are also included. The parameters obtained for each fit are presented in Table I. The errors of the slope and the intercept define the error in the estimation of filler content from I_{Exp} measurements in an unknown sample.

For a determined I_{Exp}, the error associated to the filler content, $\Delta(f_{Cu})$, can be calculated from the error of the intercept Δ(int) and the slope Δ(slope) as $\Delta(f_{Cu}) = \Delta(\mathrm{int}) + I_{Exp} \cdot \Delta(\mathrm{slope})$. The error introduced by the intercept is between 1.4% and 1.9% depending on the line, while the error introduced by the slope increases with I_{Exp}.

The performance of the procedure presented in this work was analyzed by manufacturing a sample under the same conditions as presented in the other samples with 15% of filler content. This sample was used as a test method, measuring and determining I_{Exp} for each line used in this work. The values of I_{Exp} for this sample are

presented in Fig. 5 with open symbols. The filler content was estimated using the parameters of Table 1. The following values were estimated for the lines 510.5 nm, 515.3 nm, 521.8 nm, and 529.2 nm: 13.4(±2.3)%, 14.5(±3.2)%, 14.5(±3.2)%, and 14.4(±2.4)%, respectively. The results agree with the nominal value of 15% within the experimental error.

The lines 515.3 nm and 521.8 nm exhibit the highest errors in the determination of filler content. The line 529.2 nm would be the most appropriate to determine the filler content in a sample, although it presents the highest LOD.

It is worth nothing that f_{Cu} is expressed in volume percentages with respect to the whole sample, which corresponds to a high value in atomic concentration. Then, a low LOD value can be expected.

In some works, the parameters obtained using LIBS have been related to the hardness of the material.[17–19] In particular, a linear relationship between the plasma temperature and Vickers hardness has been found on steel by LIBS tests.[18] In that work, different steel compositions were used. On the other hand, in the present work, the samples would exhibit different values of hardness in relation to the fraction of copper particles. In studies of epoxy matrix composites, it has been found that, for a given range of filler content (∼10–45% of volume fraction), the hardness can be modeled as a mixing rule. Then, it is expected that the variation of the hardness with the filler content can be fitted using a linear function. However, it is not expected that this behavior can be applied throughout the entire range of content; deviations would be expected for very low or very high content ranges. Other mechanical parameters could also be considered, such as the elastic modulus, which also presents an increase with the filler content, but differs slightly from a linear behavior. On the other hand, although several authors can use a linear function between plasma temperature and hardness, in steel[18] or graphite rubber composites,[17] for example, the values of plasma temperature are different between varied materials. However, it is worth mentioning that measuring the hardness in composite materials with inclusions of tens of microns in diameter is not easy, because the imprint of the usual techniques, such as Vickers, has dimensions of the same order. Thus, the values obtained for the hardness would not be representative of the samples. It is necessary to obtain larger imprints of the order of one millimeter and, therefore, larger samples. In this case, a possible estimation of hardness using LIBS can be especially useful.

Conclusion

In this work, the LIBS technique was used as a tool to evaluate the filler content in particulate epoxy–copper composites. Knowing the composition of some samples, it is possible to estimate the proportion of particles in an unknown sample. For the case of copper particles, the intensities of the lines show an increase with the copper volume fraction. Nonetheless, a calibration must be performed previously. Although the error in the determination seems to be significant, the procedure presented is fast and only destructive on the surface. Then, the methodology used in this work makes possible the incorporation of LIBS as a quantitative technique for the study of epoxy composites filled with metal particles, providing a method to obtain a direct estimation of the filler volume fraction. In this sense, the use of a compact device was successful. The LOD and the error sources were analyzed. On the other hand, an unknown sample was used as a test method.

In this way, a potential application is possible for a direct in situ measurement of the filler fraction through the LIBS parameters. An alternative use of LIBS can be the analysis of the dispersion of copper particles in a part of a sample, performing tests in different zones of it, or in a depth profile if the laser shot is always done in the same place.

Declaration of Conflicting Interests

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