Statistical Design of Experiments: Study of Cross-Linking Process Through the Phase-Resolved Photoacoustic Method as a Multivariable Response

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This work presents an add-on result of cross-linking using photoacoustic spectroscopy (PAS) phases in a multivariable process using the phase-resolved photoacoustic (PRPA) method. The method is tested to separate contributions from groupings –OH, –CH₂–, –CH₃, and Si–OH overtones in the range from 700 to 2600 nm. Samples of the copolymers ethylene vinyltrimethoxysilane (EVS) and grafted vinyltrimethoxysilane (VTS) on low-density polyethylene (LDPE) were prepared having concentrations (C) of 3, 5, and 7% of catalyst and temperatures (T) of 70, 80, and 90 °C. By considering the condensation reaction, the reduction of -OH groups is monitored. The PRPA analysis was carried out using the surface response methodology and results indicated the optimum point for both answers (signal and phase-resolved) and for both factors of interest (C, T). For the copolymers, it was found that C = (5.00 ± 1.14)% and T = (82.4 ± 4.3) °C, while for grafted LDPE PE, it was found that C = (4.92 ± 0.85)% and T = (80.8 ± 2.5) °C. These results agreed with the chemical analysis for gel content, which showed as the optimum point 5% of catalyst and temperature of 80 °C. Further, it is an advantage that the photoacoustic method allows one to perform a nondestructive analysis.

Index Headings: Phase-resolved photoacoustic method; Cross-linking; Factorial design; OH overtone.

INTRODUCTION

Currently, in all fields of science the possibility of attaining great amounts of numerical data has grown as the automation of experiments is implemented. In this context, the application of statistical tools is fundamental, mainly to explore and to understand the ever increasing amount of data that is originated as information from a multivariable data system.

A modern and important tool is the statistical design of experiments (SDE), or the so-called factorial design (FD) methodology,¹ applied in many basic science experiments and in technological experimental research.² However, it is still less used or explored in the fields of material science or spectroscopy. Understanding the effects of variables and the interactions between them is of extreme importance in understanding the processes that are being monitored in one determined system. When a one-varied optimization method is used, it is not possible to detect interactions between the studied variable and any other variable, for example, the stoichiometric study of simple doping (concentration), thermodynamic evolution of a property, or still grain sized control for optimization of one given physical property (such as particle size). Therefore, to optimize a property in a rational and economic style and, further, to extract from the system under study the maximum of useful information, experimental designs of experiments can be used. These are based on statistical principles and expressed through mathematical methods that seek to maximize or to minimize a given property, thus trying to keep the number of experiments to a minimum.

This paper presents a cross-linking study, prepared using the FD methodology, of two polymers for monitoring the photoacoustic phase difference between two typical absorption bands as the multivariable response. The samples under study are polyethylene (PE) films cross-linked by means of water-saturated vapor, specifically, copolymers of ethylene vinyltrimethoxysilane (EVS) and grafted vinyltrimethoxysilane (VTS) on low-density PE (LDPE). These polymeric materials combine low electrical conductivity with high heat transfer efficiency and are used worldwide as electrical insulating wires.

Photoacoustic spectroscopy (PAS)³–⁵ and Fourier transform infrared (FT-IR) PAS,⁶–⁹ being nondestructive techniques, play a basic role in the study of the composition and structure of materials in layers⁷ and solid polymers.¹⁰ PAS was recently used to better understand how optic absorption properties can be affected by the cross-linking process¹¹–¹³ and how this effect influences the thermal properties through structural change. These studies attempt to establish the best variables for the FD¹⁴ by considering the several variables used for sample preparation and using PA peak intensity as a response. The study presented here shows the add-on results of these polymers using photoacoustic phase difference in the multivariable process, but the analysis is carried out using the phase-resolved photoacoustic method (PRPA).¹³ The PRPA is used here to separate contributions from the groupings –OH, –CH₂–, –CH₃, and Si–OH overtones that are present in both cross-linked polymers in the range from 700 to 2600 nm, i.e., the near-infrared (NIR) and mid-infrared (MIR) region.

EXPERIMENTAL

Materials. Pellets of commercial copolymer (200 g) were extruded with three different concentrations of catalyst (Union Carbide Co., DBFB544480, 0.34 wt % of dibutyl-tin-dilaurate) that are used as cross-linking initiators and are triturated in the milling of knives. After that, it was pressed in the form of films (85 to 595 μm thick), conditioned in suitable containers, and kept in a freezer. The LDPE in pellet form (600 g) was kept at 80 °C for 12 h in a greenhouse and then grafted with 40 mL of VTS via reaction with 2.5 g of benzoyl peroxide, under mechanic agitation for 1 h, and was then extruded with
the same amount of catalyst, speed condition, torch rate, and temperature used for the copolymer. The final materials were triturated and pressed to form films (90 to 385 μm thick) and then conditioned in a freezer. The films were cross-linked in a glass reactor for 8 h with different controlled temperatures in a humidity-saturated atmosphere. Figures 1a and 1b show the cross-linking scheme of the EVS copolymer (hereafter called Cop) and the grafted PE (PEg), respectively.15-17 The grafting via peroxide results in a longer ramification and is therefore more mobile when compared with the EVS copolymer.

**Photoacoustic Setup.** The experimental setup for the photoacoustic spectroscopy (PA) is described elsewhere.3,12,14 In this paper, data were collected using a homemade photoacoustic configuration for the UV-VIS and mid-infrared regions. In this setup, a white light (Xe arc lamp, Oriel 68820, 1000 W) passes through a monochromator (Oriel 77250, 180 nm to 3800 nm). A mechanical chopper modulates the light and the beam goes to the PA cell. A conventional PA cell must have an optical window to allow radiation to reach the testing sample placed inside. A chopper driver (Stanford Research Systems SR 540, 1 Hz to 3 kHz) gives the pulse reference that synchronizes the PA signal (1 μV to 2 mV) collected by the microphone (Bruel & Kjaer BK 2669, 50 mV/Pa). This signal is monitored by a lock-in amplifier (EG&G Instruments, 5110), and a personal computer (PC) controls wavelength scanning and the signal detection using the usual IEEE boarding. The experiments were performed using a frequency of 20 Hz and light power of 800 W.

**Techniques. Phase-Resolved Photoacoustic Method.** The photoacoustic signal comprises amplitude and phase. The phase is independent of power and is exploited with advantage over the signal amplitude since power fluctuation has no influence on the phase but can strongly change the amplitude. Phase is dependent on depth (thermal diffusion length) and can be altered if the depth at which heat is generated is changed by the chopping frequency. Thus, one can understand the phase as the average for the thermal relaxation time of the whole chromophore within a thermal diffusion length. Furthermore, for layered samples with layers having different physical properties, the PA signal is generated having different thermal diffusion times and it causes a phase lag, Δφ, that reflects the phase difference between layers. In addition, if there are adjacent layers or different absorbing centers there will exist a specific phase φ where the signal from the lowest layer is detected.

In the phase-resolved photoacoustic method, we study a photoacoustic spectrum composed of more than one absorbing component, but in which the two components are hidden in peaks very close to each other, i.e., either absorption from two chromophores or from a two layer system (centers or layers A and B, for example). In other words, PA signals S_A(λ1) and S_B(λ2) have bands that are superimposed and centered at two wavelengths, λ1 ~ λ2, very close to each other. In principle, if the PA signal presents a phase difference Δφ = (φ_B - φ_A) ≠ 0 at a chosen wavelength, then we may be able to resolve the spectra for each component.

Modern instrumentation allows accuracy of less than 1° for phase measurement of a single spectral component. On the other hand, it is usually assumed that for most photoacoustic spectra generated by two adjacent layers or two absorbing centers having very close peak centers, the phase lag measured must be more than that of the instrument. For the case we are analyzing in this paper, the lower limit of the phase difference is assumed as Δφ > 5°. In this case, one may apply the numerical method called the phase-resolved photoacoustic method (PRPA)4,13,18,19 to separate the individual contribution from each one at a specific phase value. The PA signal, in the PRPA method, is represented in a phasic picture having a module and a phase S(λ) = S|e^{iΔφ(λ)}|, where φ is the phase of the signal at a wavelength and can be separated into two components, in-phase and quadrature, using S(λ) = [S(λ)cos(θ) + S(λ)sin(θ)].13 When layer A is minimized at φ, it is maximized at θ = φ' ± 90° and the spectrum of the layer B is isolated at φ'. Naturally, other layers, such as B, may be enhanced at θ = φ'' ± 90° and isolate the spectrum of the layer A at φ''. Therefore, this method allows one to determine the form of the spectra of some contribution and in which relative phase the signal would be found, without varying the modulation frequency. The PRPA is used here to separate contributions from the groupings —OH, CH₂—, CH₃, and Si—OH overtones for both Cop and PEg.

**Statistical Design of Experiments.** The factorial design of experiments is classified as a method of the simultaneous type, where the variables of interest that present significant influences in the response factor of the experiments are evaluated at the same time.

In this method, the variables are chosen to be studied...
(named factors) and experiments are performed at different values (say levels) of these factors. Following this, experiments are performed for all possible combinations of the selected levels. In a general way, the factorial design can be represented as \( N = b^k \), where \( N \) is the number of experiments, \( b \) is the number of levels, and \( k \) is the number of variables. In the present case, three different levels for two factors have been chosen: temperature and concentration of catalyst. Upon considering the value of \( b \) and \( k \), the number of factors and levels, this FD design can be indicated as being \( 3^2 \). This choice suggests a design of nine experiments or to perform nine different samples by combining temperature and concentration. Despite the fact that this FD is less common than the case of \( 2^k \), where the effect of the variables can be easily calculated and thus interpreted, the effect between the variables in the \( 3^2 \) FD can mostly be studied using the methodology of surface response (MSR). MSR also has no restrictions either on the number of factors or on the answers. This is a very important characteristic of MSR; also, many times a product or process must satisfy more than one criteria.\(^{1,20} \)

In the experimental designs it is common to codify the levels of the variable using signals (+) and (−). The attribution of these signals to the superior or inferior levels is made in an arbitrary manner and does not intervene with the accomplishment of the experiments or even with the interpretation of the results. In addition, this approach allows schematizing the design in the form of matrices of changeable design and makes it possible to analyze qualitative variables. This codification of variables, even though seemingly unnecessary, is of great aid when a statistical design methodology is applied, mainly because the calculations allow one to determine the influence of the studied variable and its interactions within the system under study.\(^{20} \)

**RESULTS AND DISCUSSION**

**Spectroscopic Analysis.** In order to investigate the overtones of the optical absorption band referring to hydroxyl bands and their combinations with stretching modes (vibration and rotation), we analyzed the spectral region of 700 to 2600 nm (14 285±3845 cm\(^{-1}\)) corresponding to the near- (NIR) and mid- (MIR) infrared regions. A typical photoacoustic optical absorption spectrum is shown in Fig. 2a, referring to a copolymer with concentration \( C = 5\% \) and cross-linked at temperature \( T = 80^{°}C \). This sample was coded as Cop5%80, having levels \( C, T = (0, 0) \) as presented in line 5 of Table I. All

**TABLE 1. Results of experiments with coded design 3².**

<table>
<thead>
<tr>
<th>Level ( C )</th>
<th>Level ( T )</th>
<th>( (p_2/p_1) ) ratio ( \text{Cop} )</th>
<th>( (p_2/p_1) ) ratio ( \text{PE}_g )</th>
<th>( \Delta \phi ) ( 2, 3 ) ( \text{Cop} )</th>
<th>( \Delta \phi ) ( 4, 5 ) ( \text{PE}_g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>-1</td>
<td>3.73 ± 0.21</td>
<td>0.50 ± 0.01</td>
<td>0.80 ± 0.02</td>
<td>1.05 ± 0.01</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>0.84 ± 0.04</td>
<td>0.66 ± 0.01</td>
<td>1.30 ± 0.01</td>
<td>0.92 ± 0.04</td>
</tr>
<tr>
<td>-1</td>
<td>1</td>
<td>1.00 ± 0.06</td>
<td>0.55 ± 0.01</td>
<td>1.00 ± 0.04</td>
<td>1.29 ± 0.04</td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>0.52 ± 0.06</td>
<td>1.02 ± 0.02</td>
<td>0.71 ± 0.03</td>
<td>1.10 ± 0.04</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.17 ± 0.02</td>
<td>1.49 ± 0.02</td>
<td>1.07 ± 0.04</td>
<td>1.04 ± 0.04</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0.71 ± 0.10</td>
<td>0.99 ± 0.04</td>
<td>0.71 ± 0.04</td>
<td>0.90 ± 0.03</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>1.69 ± 0.05</td>
<td>0.82 ± 0.01</td>
<td>0.71 ± 0.04</td>
<td>1.05 ± 0.04</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>1.62 ± 0.07</td>
<td>0.90 ± 0.01</td>
<td>1.07 ± 0.04</td>
<td>0.85 ± 0.10</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1.14 ± 0.04</td>
<td>0.89 ± 0.01</td>
<td>0.93 ± 0.01</td>
<td>0.95 ± 0.04</td>
</tr>
</tbody>
</table>
samples presented a similar spectrum and it was observed that no absorption band indicates directly the cross-linking effect. Thus, each peak was catalogued in order to understand the relationship between peaks and the cross-linking process. The condensation reaction mechanism involved in the cross-linking processes is considered as that shown in Figs. 1a and 1b.

Superimposed overtone intensities arising from the combinations of −OH, −CH₂, and −CH₃ groups have been previously located and studied by means of the photoacoustic spectra. It was done using a Gaussian fitting of the curves and phase differences through the phase-resolved photoacoustic method. By considering the condensation reaction (Fig. 1) one can conclude that a sample with a reduction of the absorption assigned for −OH groups would have a better cross-linking rate. Moreover, due to the difficulties of directly understanding the interaction of the variables involved in a simple way, it is imperative to use a statistical process or the factorial design.

Using PRPA, it was possible to separate the contribution of free −OH (peak 5 at 1800–1920 nm) and the first overtone of ethylene −CH₂ (peak 4 at 1760 nm); they present a phase shift of ~210° (see Fig. 2b) for Cop5%80. The PA analysis showed no separation for the stretching combination between (νCH⁴), −CH₃, and −CH₂. They are characteristic of −CH₃ (peak 7 at 2240 nm) and −CH₂ (peak 8 in the range 2300 to 2480 nm) groups as shown in Fig. 2b. On the other hand, we observed the separation of the superimposed bands, the Si-OH overtone at 1400 nm (peak 2) and combination of −CH₃ and −CH₂ at 1450 nm (peak 3), which typically leads to Δφ = ~15° for the Cop5%80. This is indicative of the existence of two absorbing centers with different times of relaxation (Fig. 2b). This result is observed for the copolymer EVS and for the grafted polyethylene in this region; all were similar to that in Fig. 2a.

**Analysis Statistics.** In Table I we present the nine coded samples of the factorial design used, where two quantitative variables in three levels are taken into consideration: concentration of the catalyst (3, 5, and 7%) and temperature (70, 80, and 90 °C). For each coded sample we have registered the answers from absorption spectra, ratio of the PA signal (p_i/p_j), and the phase difference (Δφ) between two distinct peaks resolved by PRPA. The phase difference (Δφ) is normalized to its respective number of degrees of freedom. Thus, each peak was catalogued in order to understand the relationship between peaks and the cross-linking process.

The quadratic model is the more satisfactory empirical model; also, it shows a faithful relation between variables given in the form

\[ \hat{y} = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2 \]  

This means that this quadratic model estimates the ratios of the signal PA and the phase difference in each point of the FD, for each sample, by means of the equations:

\[
\hat{y}_{\text{Cop}} = 0.074 - 0.19C - 0.51T + 1.20C^2 + 0.59T^2 + 0.54CT
\]

\[
\hat{y}_{\text{Peg}} = 1.31 + 0.15C + 0.015T - 0.45C^2 - 0.22T^2 + 0.005CT
\]

\[
\hat{y}_{\text{Cop}} = 1.05 - 0.065C + 0.070T + 0.014C^2 - 0.34T^2 + 0.005CT
\]

\[
\hat{y}_{\text{Peg}} = 0.93 - 0.010C - 0.070T + 0.12C^2 + 0.005T^2 + 0.085CT
\]

The calculation of the uncertainties in the estimation of the elements of vector b, or its confidence intervals, can be evaluated using the distribution t and the equation \[ b_i \pm t_{n-p} \sigma \] (error standard of \( b_i \)). Here, the index “n−p” is the number of degrees of freedom of t or the matrix equation \( V(b) = (X'X)^{-1}\sigma^2 \), where \( \sigma^2 \) is the population variance.

The residual analysis is drawn in Table II for both copolymer EVS and grafted Pe_g. In this table we tabulate the analysis of variance (ANOVA) for the PA signal ratios and phase shift from PRPA separation based on the presented quadratic model, where the argument \( \hat{y} \) value for the source Model Σ is calculated for C and T using Eqs. 3 through 6. The average \( \hat{y} \) is obtained from Table I by averaging the two columns, one for the ratio (p_i/p_j) and the other for the phase separation (\( \Delta\phi(i, j) \)). In the source Residual Σ of Table II, the individual y are the experimental values for each combination (C_i, T_j) given in Table I. Yet, in the last column of Table II is tabulated the so-called mean squares (MQs), evaluated from the ratio of the sum of squares (second column) divided by its respective number of degrees of freedom (third column). The source Total Σ of Table II is the estimated approach for the mean error squared that overcomes when using the regression equation to foresee the value y corresponding to one specific value of C and T.

The random feature of the experiment is verified by the normal graph of the residues shown in Fig. 3a for Eq. 3 referring to Cop and in Fig. 3b the same but for Eq. 4 for the Peg sample, given as an example. From this plot, a homogeneous distribution of points around the traced straight line is observed. This means that a random feature for the experiments is being found, which demonstrates that the quadratic model adjusts very well with the design of the experiment.

Substituting the values of \( SQ_M \) (sum of squares of Model Σ) and \( SQ_T \) (sum of square Total Σ) of Table II in the equation \( R^2 = SQ_M/SQ_T = \Sigma(y_i - \bar{y})^2/\Sigma(y_i - \bar{y})^2 \), one can calculate \( R^2_{\text{Cop}} = 0.89 \) and \( R^2_{\text{Peg}} = 0.76 \) for Eqs. 3 and 4. In the same way, we evaluate \( R^2_{\text{Cop}} = 0.89 \) and \( R^2_{\text{Peg}} = 0.61 \) for Eqs. 5 and 6, which means that almost 80% of the total variation around the average is explained.
by the regressions, remaining near 20% for the residues. The consequence of the choice of the quadratic model is the better agreement with data if it is compared to the linear model, since the values foreseen in the regression are drawn as lines where the response measured figures a constant value for both the signal ratio and phase difference. Figures 5a and 5c show this feature for the Cop and Figs. 5b and 5d show the same but for the PEg. It is seen that these level curves follow the same pattern for the intensity ratios, seeming to diverge from the minimum level with a ratio of ~0.03 for Cop and to converge toward the maximum level of ~1.30 for PEg. Moreover, when the response is the phase difference, the level curve for the EVS copolymer has the characteristic of a saddle point with a level close to 1.05 and for the PEg the phase difference converges to a region of lower values with level of ~0.8.

Now, returning to the point of interest, that is, monitoring the bands of absorption of the -OH groups, by following a reduction of the -OH for the case of EVS copolymer when we analyze the ratio peak2/peak3 (±OH/ \[ \text{CH}_2 \]) as response, we are interested in the smallest value (minimum point) that represents the optimum point. In Fig. 5a this point is situated approximately in \( X_1 = 0 \) (level 0 for \( C \) and \( X_2 = 0.5 \) (level 0.5 for \( T \)), which means a concentration close to 5% of catalyst and a temperature of cross-linking near 85 °C. For the PEg samples, where the ratio peak4/peak5 (±CH\(_2\)/-OH) is analyzed, one wishes to find the largest value (maximum point), and this result is shown in Fig. 5b. This maximum is found at approximately \( X_1 = 0.17 \) (level 0.17 for \( C \) and \( X_2 = 0 \) (level 0 for \( T \)), or catalyst concentration approaching 5.35% and temperature reaching 80 °C, respectively.

For the case where the response variable to be analyzed is the phase difference, we use the same indirect analysis as that for the ratios between two absorption peaks. Thus, the phase difference is calculated considering the relative phases using the expression \( \Delta \varphi = |\varphi_j - \varphi_k|_{\text{sample}} - |\varphi_j - \varphi_k|_{\text{base}} \), which corresponds to the signal ratio \( S = |(S_j / S_k)_{\text{sample}} - (S_j / S_k)_{\text{base}}| \). As the phase differences for the peaks in the NIR and MIR region were always evaluated in module, the region of best cross-linking for the variables \( C \) and \( T \), shown in Fig. 5c for the EVS copolymer and Fig. 5d for the PE grafted with VTS, is the region of the smaller difference of phase.

Although the answer in the algorithm using the phase difference is found to always show a characteristic surface of contour, and likewise a saddle point for the EVS copolymer (Fig. 5c), we used the same convergence cri-

**TABLE II. ANOVA.**

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares (p2/p3)</th>
<th>Degree free</th>
<th>Mean square (p2/p3) and ( \Delta \varphi_{(2, 3)} )</th>
<th>Degree free</th>
<th>Mean square (p4/p5) and ( \Delta \varphi_{(2, 3)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model ( \Sigma (y_i - y)^2 )</td>
<td>0.63</td>
<td>0.32</td>
<td>0.13</td>
<td>0.064</td>
<td></td>
</tr>
<tr>
<td>Residual ( \Sigma (y_i - \hat{y})^2 )</td>
<td>0.075</td>
<td>0.023</td>
<td>0.025</td>
<td>0.006</td>
<td></td>
</tr>
<tr>
<td>Total ( \Sigma (y_i - y)^2 )</td>
<td>0.71</td>
<td>0.34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Grafted VTS on LDPE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model ( \Sigma (y_i - y)^2 )</td>
<td>6.58</td>
<td>0.086</td>
<td>1.32</td>
<td>0.017</td>
<td></td>
</tr>
<tr>
<td>Residual ( \Sigma (y_i - \hat{y})^2 )</td>
<td>2.13</td>
<td>0.0053</td>
<td>0.71</td>
<td>0.0018</td>
<td></td>
</tr>
<tr>
<td>Total ( \Sigma (y_i - y)^2 )</td>
<td>8.71</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* = total number of observations (experiments) \( y_i \) in Eq. 1 and Table I, while \( p = \) total number of parameters \( b_i \) in Eq. 2.

![Image](image-url)
Fig. 4. Surface response for the EVS copolymer: (a) PA intensity ratio for peak 2/peak 3 and (c) phase difference $|\phi_2 - \phi_3|$; and surface response for the grafted PE with VTS: (b) PA intensity ratio for peak 4/peak 5 and (d) phase difference $|\phi_4 - \phi_5|$.

teron as that discussed for the intensity ratios, choosing the relative minimum for the variable $X_1$ (catalyst). Following this, the response $|\phi_2 - \phi_3|$ equivalent to the ratio $[-\text{OH}]/(n\text{CH}_1 - \text{CH}_2 - \text{CH}_3)$ for the Cop is analyzed and the best cross-linking rate might be near $X_1 = 0.25$ (catalyst $\sim 5.5\%$) and $X_2 = 0.10$ (temperature $\sim 81$ °C), as shown in Fig. 5c. Similarly, the response for PE with $|\phi_4 - \phi_5|$ equivalent to the ratio $[-\text{OH}/\text{CH}_2 -]$ was found to be $X_1 = 0.25$ (catalyst $\sim 5.5\%$) and $X_2$ between 0.55 and 0.90 ($T \sim 80-90$ °C), as seen in Fig. 5d.

To summarize these results for all samples, ratios between intensities and the differences of phase for each peak are shown in Table III. Remember that results considering peak ratios peak 1/peak 2 (equivalent to the ratio $[-\text{CH}_2 - \text{CH}_3]/[-\text{OH}])$ for both variables. A simple question that arises here is how one can assure that 5% of the catalyst is the ideal instead of 5.5% or 6.0% if in the sampling designed there are no such values for these catalyst percentages. The answer, of course, is guaranteed by the MSR algorithm.

In a recent paper, the usage of the ratio between PA signals was discussed without using the FD methodology and some of those results were reevaluated by these methods of optimization and are summarized here in Table III. This is retrieved having the objective of comparing results with those found from the phase-resolved photothermal acoustic method (PRPA) and so forth to find the optimum point with more precision. In the case where the peaks superimposed are deconvoluted through Gaussian fitting, it is necessary to perform an extra calculation, which may lead to the possibility of greater uncertainty (the deconvolution may not be well adjusted). In another way, when these peaks are separated directly by means of the PRPA method, one has the value of the phase difference for the mixed peak. The disadvantage of this PRPA procedure is the existing limit in the phase difference between the two superimposed peaks that was already mentioned in the Introduction of this paper, if this threshold phase difference is $\Delta \phi \leq 5^\circ$ is dominant. Thus, the PRPA incapacity to separate them comes up once instrumental accuracy is of the order of $1^\circ$ and phase data noise can be greater than that.

**CONCLUSION**

The experimental study involving two factors and three levels resulted in the characterization of the influence of
Fig. 5. Curves of level for EVS copolymer: (a) PA intensity ratio for peak2/peak3 and (c) phase difference $|\phi_2 - \phi_3|$; and for the grafted PE with VTS: (b) PA intensity ratio for peak4/peak5 and (d) phase difference $|\phi_4 - \phi_5|$.

TABLE III. Summary for the optimum point.

<table>
<thead>
<tr>
<th></th>
<th>Optimum point (or reduction of the –OH groups)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Results from signal PA</td>
<td>Results from phase-resolved PRPA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Maximum</td>
<td>Minimum</td>
<td>Minimum (module)</td>
</tr>
<tr>
<td></td>
<td>$X_1$ ($C%$)</td>
<td>$X_2$ ($T\degree C$)</td>
<td>$X_1$ ($C%$)</td>
</tr>
<tr>
<td></td>
<td>$X_2$ ($T\degree C$)</td>
<td></td>
<td>$X_2$ ($T\degree C$)</td>
</tr>
<tr>
<td>EVS Copolymer</td>
<td>$\Delta \phi (1, 2)$</td>
<td>$\Delta \phi (2, 3)$</td>
<td>$\Delta \phi (1, 2)$</td>
</tr>
<tr>
<td>peak1/peak2</td>
<td>0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>(79.5)</td>
<td>(85)</td>
<td></td>
</tr>
<tr>
<td>peak4/peak5</td>
<td>$\Delta \phi (4, 5)$</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>(90)</td>
<td>(6.5)</td>
<td>(80)</td>
</tr>
<tr>
<td>Grafted PE with VTS</td>
<td>$\Delta \phi (1, 2)$</td>
<td>$\Delta \phi (2, 3)$</td>
<td>$\Delta \phi (1, 2)$</td>
</tr>
<tr>
<td>peak1/peak2</td>
<td>0.05</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>(5.1)</td>
<td>(80)</td>
<td>(4.3)</td>
<td>(81.3)</td>
</tr>
<tr>
<td>peak4/peak5</td>
<td>$\Delta \phi (4, 5)$</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>(0.2)</td>
<td>(80.1)</td>
<td>(5.7)</td>
<td>(85.5)</td>
</tr>
</tbody>
</table>

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factors on the response of interest with sufficient precision. All experiments were done in accordance with a systematic design of samples. This way of proceeding is believed to be superior to the way that prevails in most research laboratories, in which researchers seek to optimize a specific property using a conventional one-dimensional variable such as temperature, concentration, or magnetic field that leads to a bi-dimensional plot instead of a multivariate surface plot.

The results for both analyses, PAS intensity ratio and phase difference from PRPA, for the samples EVS copolymer and LDPE grafted with VTS prepared with factorial design $^{3}$ revealed sufficiently satisfactory results and indicated the optimum point for both answers (signal and phase difference) and for both factors of interest ($C$, $T$). For the copolymer Cop, we found that $C = (5.00 \pm 1.14)\%$, with a percentile error $\delta \sim 23\%$ and $T = (82.4 \pm 4.3) \degree C$ with a percentile error $\delta \sim 5.2\%$, while for grafted PE it was found that $C = (4.92 \pm 0.85)\%$ with an error $\delta \sim 17\%$ and $T = (80.8 \pm 2.5) \degree C$ with error $\delta \sim 3.1\%$, being the percentile relative deviation below 25% for all analyzed polymers. These results agreed with the destructive chemical analysis for gel content, which showed as the optimum point of cross-linking the values 5% of catalyst and temperature of 80 $\degree$C, leaving the advantage that the photoacoustic method allows one to perform a nondestructive analysis.

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