Study of cross-linking process in grafted polyethylene and ethylene based copolymer using a phase resolved photoacoustic method

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In this work, the phase resolved photoacoustic method has been employed to monitor water saturated vapor cross linking in both copolymer and grafted polyethylene. The overtone bands and stretching frequencies combinations of the –Si–OH, =CH2, –CH3, and –CH2–CH3 were monitored and analyzed accordingly to a 32 factorial design with nine samples. The results showed that the cross-linking processes were more efficient when the samples were prepared at 80 °C with the catalyst in the concentration range between 3% and 5% for grafted PE, while 70 °C was the best temperature to obtain copolymer. © 2003 American Institute of Physics.

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I. INTRODUCTION

Polyethylene (PE) is used worldwide as electrical insulating wire, especially in applications that need high temperature operation. The physical properties of cross-linked PE will be dependent on the cross-linking rate. PE is cross linked by means of Sioplas technology. In this method, silane groups are cross linked under water vapor. The alkoxy group is converted into silanol group and undergoes a condensation reaction with a hydroxyl in an adjacent chain to form “Si–O–Si” type network.1

The copolymer from ethylene vinyl trimethoxysilane (EVS) and the grafted vinyl trimethoxysilane (VTS) on low density polyethylene (LDPE) when cross linked by means of water-saturated vapor combine low electrical conductivity with high heat transfer efficiency.2,3 These materials are especially indicated for applications that require high temperature conditions.

In the last few years, the properties of silane grafted PE have been the subject of many studies investigating the cross-linking kinetics4 and also the morphological changes induced in the polymer chain.5

In this work it was used the above discussed condensation reaction as the main base for an indirect analysis of the cross-linking process. It was applied to the phase resolved photoacoustic spectroscopy method6 (PR-PAS) in the near infrared (NIR, 800–1600 nm) and medium infrared (MIR, 1600–3200 nm). This range contains overtones of hydroxyl bonds and their combination with stretching modes of CH.

II. EXPERIMENT

A. Samples preparation

Commercial pellets of EVS copolymer (200 g) were extruded with three different concentrations of catalyst (Union Carbide Co., DBFB544480, 0.34 wt. % laurate of dibutyl-tin) and were hot pressed in order to perform the copolymer films (85–595 μm thick). The pellets of low density polyethylene (LDPE) (600 g) were kept in an oven at 80 °C for 12 h. After that, they were grafted with 40 ml of vinyltrimethoxysilane (VTS) whose reaction was initiated by 2.5 g of benzoyl peroxide by stirring the solution during 1 h.

The grafted LDPE was then extruded using the same amount of catalyst as in the EVS copolymer described above, also keeping the same stirring speed, torch rate, and temperature. The final grafted LDPE, after being grounded, was hot pressed to make films (90–385 μm thick), which were maintained in adequate recipients and kept in a freezer before the cross-linking process.

The grafted (LDPE + VTS) polymer (hereafter named as PEg) and the EVS copolymer (named as Cop) films were cross linked in humidity saturated atmosphere in a glass reactor for 8 h. The process was performed in thermostatic conditions.

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Table I. Sample factorial design 32 T=temperature and C=concentration.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Cop</th>
<th>PEg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variables:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T(°C) ⇒</td>
<td>B</td>
<td>a</td>
</tr>
<tr>
<td>C (wt%) ↓</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>5</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>
controlled bath at different temperatures. In this way a $3^2$ factorial planning design has been applied, resulting in nine experiments for each set of sample, as shown in Table I. For example, samples were coded as Pe$_g$3%70 and Cop7%90.

The overall cross-linking mechanism of silane grafted PE and EVS copolymer are depicted in Figs. 1~a~ and 1~b~,4,5 respectively. The silane cross linking of grafted PE results in a longer and more mobile network seen in Fig. 1~a~ when compared with the EVS copolymer Fig. 1~b~.

### III. RESULTS AND DISCUSSION

The spectral range of our interest here is 700–2600 nm (14 285–3845 cm$^{-1}$) corresponding to NIR and MIR region, where the absorption bands are mainly due to overtones and combination of the fundamental modes of vibration and rotational bands. By means of the PAS method, in the region 1050–2600 nm (9523–3846 cm$^{-1}$) it was possible to identify and assign the absorption bands for the silane-grafted polyethylene and EVS copolymer, referring to the overtones and their combination with stretching modes.

The superimposed overtones from the combinations of groups –OH, –CH$_2$–, and –CH$_3$ were located and studied by means of intensities and phases; see Fig. 3 for PE$_g$5%80. Using PRPA, it was possible to separate the contribution of free OH and the first overtone of the methylene –CH$_2$–, which presented phase shift ~23°, see Fig. 4 for Cop7%70. PA analysis showed no separation for the stretching combination of CH–, characteristic of –CH$_2$– and –CH$_3$ groups, in the range of 2300–2480 nm, shown in Fig. 4 with no phase shift.

It was observed that there is no phase difference for both PE$_g$ and Cop samples in this range. Results showed that peak 2 (Si–OH overtone at 1300 nm) and peak 3 (combination of –CH$_2$– and –CH$_3$ at 1400 nm) have a phase difference of 10° for PE$_g$ 7%70, typically, indicating the existence of two absorbing center, with different relaxation time. Figure 4 shows a typical phase difference for Cop7%70, for peaks 4 and 5 (~23°), while Fig. 5 presents the PR-PAS result for the PE$_g$ 7%70 sample. Using a multivariable statistic algorithm, the resolved

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**FIG. 1.** Mechanism of hydrolysis and cross-linking formation through the condensation reaction of silanol groups: (a) grafted polyethylene and (b) ethylene vinyltrimethoxysilane (EVS) copolymer.

**FIG. 2.** Phasorial diagram for phase resolved PAS.

**FIG. 3.** Typical PA spectra of PE$_g$5%80.

**FIG. 4.** PA phase difference for peaks 4, 5 (~23°) and for 7 and 8 (~0°).
phase difference $\Delta \varphi$ was used as the response vector $\Delta \varphi(\lambda)$ in the analysis.\(^8\) The algorithm consists in solving $(X_{i,j})^T \Delta \varphi(\lambda) = b_i$, where $X_{i,j}$ is the planning matrix having unity elements $+1$, $0$, and $-1$, according to the level of $(C,T)$. The vector $b_i$ gives the whole statistic effect for the average of PA resolved phases, for each individual variable, and for the interaction effects involving two or more variables. Having $X_{i,j}$ one can calculate the effect vector $b_i$, being the average phase difference effect $b_0 = \Sigma [(\Delta \varphi(\lambda))/3]$, $b_1$, $b_2$, $b_3 = b_{11}$, $b_4 = b_{22}$, $b_5 = b_{12}$ are either the single or interaction effect between variables, respectively. It results in quadratic surface response given as $M = b_0 + b_1 * C + b_2 * T + b_{11} * C^2 + b_{22} * T^2 + b_{12} * (C * T)$, and coefficients are given in Table II.

The analysis from PR-PAS data showed the capability of evaluating the cross-linking rate in grafted PE with VTS and also in the copolymer EVS, by analyzing the overtone bands. It has also indicated that, in the set of samples used, the best variables for cross linking were 70 and 80 °C for both Cop and PE\(_g\), while the best catalyst concentrations were 3% for PE\(_g\) and from 5% to 7% for Cop.

In Table III we summarize the overall findings on phase separation for both PE\(_g\) and Cop, in separating the peaks 1 (overtone $-\text{CH}_2$ and $-\text{CH}_3$), 2 (first ov free OH) and 3

TABLE III. Surface response $M$ as a function of C and T.

<table>
<thead>
<tr>
<th>Variant response</th>
<th>$\Delta \varphi(1,2)$</th>
<th>$\Delta \varphi(2,3)$</th>
<th>$\Delta \varphi(4,5)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE(_g) Catalyst ($\pm$ 1 wt%)</td>
<td>2.5</td>
<td>4.0</td>
<td>5.2</td>
</tr>
<tr>
<td>Temperature ($\pm$ 5 °C)</td>
<td>75.2</td>
<td>75.8</td>
<td>80.8</td>
</tr>
<tr>
<td>Cop Catalyst ($\pm$ 1 wt%)</td>
<td>3.0</td>
<td>5.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Temperature ($\pm$ 5 °C)</td>
<td>68.0</td>
<td>68.0</td>
<td>70.0</td>
</tr>
</tbody>
</table>

FIG. 5. PR-PAS separation of peaks 4 and 5 of PE\(_g\) 7%70.

($\nu_{\text{CH}_2}$ $-\text{CH}_2$ and $-\text{CH}_3$) for near infrared range. Also, it was possible to separate peaks 4 (first ov $-\text{CH}_2$) and 5 (combination of free OH) in the medium infrared range.

IV. CONCLUSION

In conclusion, by comparing the efficiency of the variables in the cross-linking process, it was found that the most significative variable for PE\(_g\) was the catalyst concentration, followed by temperature. On the other hand, for Cop samples temperature was more influential than catalyst concentration. Yet, based upon phase resolved separation of peaks 1–2, 2–3, 4–5, and 5–7, for all samples, the best value for temperature for PE\(_g\) is in the range between 75 and 80 °C with catalyst concentration between 2.5 and 5.2 wt.%. In the case of Cop samples these variables vary from 68 to 70 °C and from 3 to 7.5 wt.%. It appears, therefore, that the method is less sensitive for the catalyst concentration variable when applied to Cop.

ACKNOWLEDGMENTS

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