POLYCHLOROPRENE/NATURAL RUBBER BLEND

DEGRADATION BY A PHOTO-FENTON PROCESS

Adonilson R. Freitas, Adley F. Rubira, Edvani C. Muniz

GMPC – Grupo de Materiais Poliméricos e Compósitos
Departamento de Química – UEM – Av. Colombo, 5790. Code 87020-900 Maringá – Paraná – Brazil – adonilsonfreitas@yahoo.com.br; afrubira@uem.br; emuniz@uem.br.

The effect of FeCl$_3$.6H$_2$O in degradation of polychloroprene/natural rubber blend (PCP/NR) (50/50) was studied by viscometry in an Ubbelohde capillary viscometer. The effects of the variables concentration of blend (Cp), temperature (T) and presence of polychromatic light (L) on the degradation process were available using a $2^3$ factorial design. The miscibility of PCP/NR blends (changing the relative composition of each component) was evaluated from the dependence of efflux time vs. conc. of PCP. The photo-degradation rate constant was determined through solution efflux time data. FTIR and GC-MS spectroscopy were used to characterize the degradation products. It was verified that the polymers are miscible in all concentration range. From the efflux time data, it was verified that, in contrast to Cp and light exposure which play a significant role in PCP/NR degradation, the temperature does not affect the degradation of such blend. Efflux time data characterized the reaction as being second-order kinetics related to the Cp input. Exposure of PCP/NR blend to polychromatic light in presence of FeCl$_3$.6H$_2$O induces structural changes in the polymers for instance, decrease in C=C bonds and appearing of conjugated carbonyl bands as well as the hydroxyl bands, as observed FTIR and GC-MS.

1. Introduction

In the last years polymer blends have attracted the attention of materials researchers. The properties of polymers can be modified to a specific requirement by blending two or more polymers [1,2]. However, most of the polymers are non-biodegradable and their blends, often, are non-biodegradable what could be an additional environmental problem [3].

More than a century ago, Fenton discovered that mixtures of ferrous ions and hydrogen peroxide could oxidize many organic compounds. The called-Fenton reaction became widely studied and presents potential uses in pollutant treatment/degradation and in many other fields [4].

The aim of this work was to investigate the degradation of polychloroprene / natural rubber (PCP/NR) blend (50/50) in the presence of polychromatic light and FeCl$_3$.6H$_2$O.

2. Experimental

2.1 Materials

Commercial polychloroprene rubber samples (Proquimil, Brazil) and FeCl$_3$.6H$_2$O (Riedel-de-Haén, Germany) was used without further purification. Natural rubber (NR, Heveas Brasiliensis) was purified by precipitation from toluene (3% w/v) into excess of ethanol. The precipitated were dried at room temperature and under reduced pressure. The dried samples were stored at -4 °C in the dark to prevent oxidation. Analytical grade toluene as a solvent was used after distillation. A commercial fluorescent lamp (low pressure mercury and argon stream, 9 W) was used as the polychromatic light source.

2.2 Miscibility available at PCP and NR polymers in the blend.

Binary solution of PCP and NR was prepared by mixing the solutions of respective polymers having different weight ratios in toluene at ambient temperature. Each blend solution was stirred by 24 hours in the dark. Efflux time measurements of each PCP/NR blend solution were performed in suspended-level of an Ubbelohde glass capillary viscometer, Cannon (100/E534), at 25 °C.

2.3 Efflux time measures to follow the degradation

Stock solutions (5% w/v) PCP/NR blend and FeCl$_3$.6H$_2$O were prepared in toluene, from film previously prepared. The film was prepared in proportion (50/50) in mass of each polymer. In the viscometer a homogeneous mix of 50/50 PCP/NR and FeCl$_3$.6H$_2$O was obtained. The efflux time of the (50/50) PCP/NR blend/FeCl$_3$.6H$_2$O solution was measured in an Ubbelohde capillary viscometer, Cannon (100/E534). The efflux time were measured as function of reaction time (time counts after addition of FeCl$_3$.6H$_2$O) to each ratio of blend/FeCl$_3$.6H$_2$O, according to the Table 1. In this way, a $2^3$ experimental design was performed where the input parameters, polymer concentration (Cp), temperature (T) and light (L) were maintained in high (+) or low (-) levels. The fixed values of Cp, T and L are described in Table 1.
So, from this 2^3 factorial design, eight different experiments were carried out, as described in Table 2.

<table>
<thead>
<tr>
<th>Runs</th>
<th>Inputs</th>
<th>Output</th>
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<tbody>
<tr>
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<td>8</td>
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Values experimentally obtained at \(T_{E_{1/2}}\).

### 2.4. Photo-degradation reaction kinetics

Viscometry data was also used to determine the degradation rate constant, defined as being the change in the concentration of a reactant or product per unit of time. The reaction order and rate constant must be determined experimentally [4]. In this work, the reaction order was available from the data collected using normalised efflux time measurements.

### 2.4 FTIR

Stock solutions of PCP/NR and FeCl\(_3\cdot6\)H\(_2\)O were mixed to obtain the concentration of run 6 (Table 2). After exposed to polychromatic light during different periods of time, the solution was dropped onto a surface of a polished NaCl crystal. Cast films were obtained under reduced pressure in the dark at room temperature. So, using a Bomem FTIR spectrometer, model MB-100, infrared spectra were obtained.

### 2.5 CG-MS

The CG-MS was performed in a Shimadzu gas chromatograph coupled with a mass selective detector model QP2000A. The GC column was a capillary column SE-30, 60 m length and 0.25 mm diameter, coated with poly(dimethyl siloxane). The injection was set at 80 °C, while the temperature of column was programmed to stand at 40 °C (during 6 min) and then change to 150 °C at heating rate of 10 °C min\(^{-1}\). Helium flowing at 30 mL min\(^{-1}\) was used as carrier gas. In this study, the run 3 condition was used after 48 hours of stirring in constant light exposure.

### 3. Discussions

It is well known that plots of absolute viscosity vs composition deviate from linearity according to the degree of compatibility of polymers. Plots for incompatible systems are linear whereas for incompatibles systems the plots are S-type, indicating two phase formation with reversal of phases at the intermediate composition [8,9]. A linear straight line was obtained when the absolute viscosity vs fraction of NR in the blend was fitted. Then the polymers are miscible in all concentration range [2]. In the input ranges investigated (Table 1), strong contributions of polymer concentration (Cp) and light (L) to the photo-degradation process were observed, in contrast to temperature (T), which did not have any significant influence. On the other hand, the degradation of PCP/NR depends on FeCl\(_3\cdot6\)H\(_2\)O added as much as the presence of light. In absence of such light the degradation occurs slower so that in presence of polychromatic light the decrease in the efflux time was almost four times larger than in the absence of light. Therefore, the presence of FeCl\(_3\cdot6\)H\(_2\)O is crucial for the PCP/NR photo-degradation. So, it was characterized as a predominantly Photo-Fenton process. Efflux time data characterized the reaction as being second-order kinetics related to the Cp input. Exposure of 50/50 PCP/NR blend to polychromatic light in presence of FeCl\(_3\cdot6\)H\(_2\)O induces structural changes in the polymers for instance, decrease in amount of C=C bonds and appearing of conjugated carbonyl bands as well as the hydroxyl bands, as observed FTIR and GC-MS.

### 4. Conclusions

It was verified that PCP and NR are miscible in all concentration range. From the efflux time data, it was verified that, in contrast to Cp and light exposure which play significant role in PCP/NR degradation, the temperature does not affect the degradation of such blend. Efflux time data characterized the reaction as being second-order kinetics related to the Cp input. Exposure of PCP/NR blend to polychromatic light in presence of FeCl\(_3\cdot6\)H\(_2\)O induces structural changes in the polymers such as decrease in the amount of C=C bonds and appearing of conjugated >C=O bands as well as the -OH bands, as observed FTIR and GC-MS.

### 5. Acknowledgements

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### 6. References