

## PHOTODEGRADATION AND CHARACTERIZATION OF POLY(ETHYLENE OXIDE) / MONTMORILLONITE COMPOSITE FILMS

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### Abstract

*Poly(ethylene oxide) (PEO) composites with different concentrations of SWy-1 montmorillonite clay were prepared by solution intercalation method. Thin films of composites obtained by solvent evaporation were exposed to UV-irradiation. The photodegradation was monitored by FTIR and the chain scission reaction was confirmed by measurement of average molecular weights using size exclusion chromatography (SEC) method. The rate of oxidation of PEO was much faster than that of composites (PEO/SWy-1). The SWy-1 clay can be considered as stabilizer against UV irradiation. The stabilization mode of the clay may be explained on the ability of SWy-1 not only scatter the incident light but also to absorb the UV light instead of the PEO, thus minimizing the degradation rate of composites.*

### 1 Introduction

Polymer-clay nanocomposites are a new class of materials derivate of clay nanoparticles dispersed in the polymer matrix and have at least one of its dimensions in the nanometer range. The polymer-clay nanocomposites can provide, at very low silicate contents, improvements in physicals, chemicals and mechanicals properties<sup>[1],[2]</sup>.

When preparing a polymer-clay nanocomposite, the most commonly used clay is montmorillonite (MMT). Its structure type is 2:1, in other words, it consists of packets of two tetrahedral silicate layers of silicon and a central octahedral silicate layer of magnesium or aluminum. The isomorphic substitution within the layers, for example Al<sup>3+</sup> replaced by Mg<sup>2+</sup> or Fe<sup>2+</sup>, generate excess of negative charge which is balanced by exchangeable cations (Na<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>) located into the space between layers of clay<sup>[2],[3],[4]</sup>.

The preparation method of nanocomposites can be classified into three types: intercalation polymerization, which is intercalated between layers silicate one or more monomers and subsequent polymerization; polymer intercalation by the solution method; and polymer intercalation by the melt method. The solution intercalation method is commonly used by water soluble polymer, such as poly(ethylene oxide) (PEO)<sup>[5],[6]</sup>.

The photo-oxidative degradation is critical to polymer materials in their process and usage. It is even the case in polymer layered silicate composites. Photooxidation is a serious factor of concern and its effect on pure polymers has been the subject of several studies<sup>[7],[8]</sup>. The

mechanism of PEO photodegradation, both in the solid state and in aqueous solutions was described and discussed in detail by Morlat and Gardette<sup>[9],[10]</sup>. Despite the numerous reports on polymer layered silicates, very little attention has been paid to their photodegradation behavior<sup>[11],[12],[13]</sup>.

In the present work, the effect of UV-irradiation on PEO/SWy-1 nanocomposites has been investigated.

## 2. EXPERIMENTAL

### 2.1. Materials

The clay mineral used in this work was the montmorillonite clay SWy-1/Na<sup>+</sup> supplied by Source Clays Repository of the Clay Minerals Society, University of Missouri, Columbia, Mi. PEO was supplied by Sigma Aldrich (average molar mass ~100.000).

### 2.2. Composites preparation

The films were prepared by intercalation method. Suspensions with different concentrations of clay (0.5%, 1.0%, 2.5% and 5.0%) were stirred in 10 mL of the water deionised water and passed through a purification system Easypure® Rodi for 24 hours. Afterwards, an aqueous solution of PEO (1%, w/v) was added to the clay suspensions. The clay-PEO solutions containing different amount of SWy-1 were poured onto glass plates and dried at 37 °C. The mixture was then heat-pressed in the hydraulic press between two aluminium supports for 1 min at 100 °C and 3.5 TON. The films were peeled off the aluminium support and stored.

### 2.3. Analysis

The intercalated compounds were characterized by X-ray diffraction (XRD) on a Enraf-Nonius Kappa CCD diffractometer (Cu, radiation  $\lambda = 0.154$  nm) at 50 kV, 100 mA.

The influence of clay in the stability of PEO during thermal degradation was studied by Thermogravimetric analysis (TG) using TA Instruments thermobalance (SDT – 600). The melting and polymer crystallization processes was accompanied by differential scanning calorimetric (DSC) (TA Instruments, model DSC-Q 10).

Photodegradation was followed by Fourier transform infrared spectroscopy (FTIR) (Bomem-100 MB Series spectrometer) with Attenuated Total Reflection (ATR) unit (Specac, Co). Average molar masses were determined by size exclusion chromatography (SEC) on a Shimadzu LC-10 AD chromatographic system with a Shimadzu RID – 6A refractive index detector. Irradiated film samples were dissolved in deionized water and passed through a purification system Easypure® Rodi and filtered using filters of 0.45  $\mu\text{m}$  of the sample solutions were injected in set of three OHPAK KB-806M columns. Deionized water and passed through a purification system Easypure® Rodi was used as the eluent at a flow rate of 1 ml min<sup>-1</sup>. Narrow-distribution poly(ethylene oxide) standards (American Polymer Standards Corp.) were used for calibration.

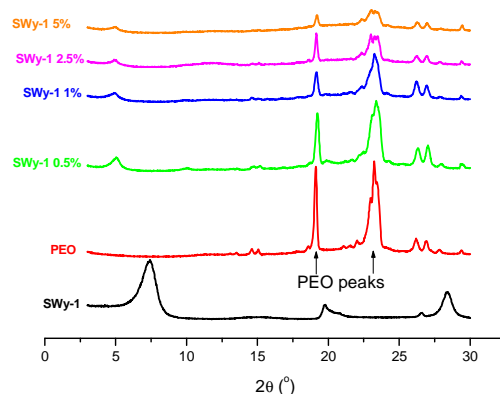
### 2.4. UV irradiation

The films were irradiated with UV light in irradiation chamber containing 16 UV germicidal lamps (total power 96 W) at 40 °C. The lamps emitted predominantly 254-nm wavelength and the photon flux was  $1.78 \times 10^{21}$  photons/m<sup>2</sup>s. The photon flux and emission spectre were determined using the equation described by Neumann *et al*<sup>[14]</sup> and spectroradiometer SPR-01 (Luzchem), respectively.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of PEO/SWy-1 composites

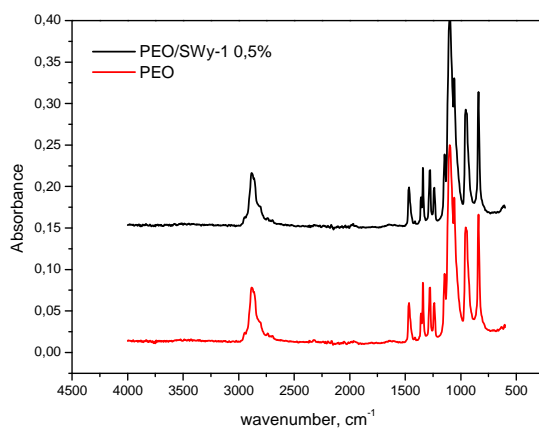
The structure of the composites with different amounts of SWy-1 was studied by X-ray diffraction. Fig. 1 shows the X-ray diffraction (XRD) patterns of SWy-1 clay, pristine PEO and PEO/SWy-1 composites.



**Figure 1:** X-ray diffraction patterns of SWy-1, pristine PEO and PEO/SWy-1 composites.

The interlayer distance was calculated using the Bragg Equation ( $n\lambda = 2d \sin \theta$ ). The diffractograms of SWy-1 shows a peak at  $2\theta = 7.4^\circ$ , which corresponds to an interlayer distance of about 12 Å corresponding to the hydrated sample containing a monolayer of  $H_2O$ <sup>[15]</sup>. In the case of composites PEO/SWy-1 there is a peak shift to lower values of  $2\theta$  ( $\sim 5^\circ$ ) resulting in an increase in the interlayer distance of about 18 Å.

FTIR spectra of pristine PEO is presents in Fig. 2. As can be seen, the pristine PEO exhibits a broad band at  $2881\text{ cm}^{-1}$  due to the symmetric stretching of the  $-CH$  bond (from the aliphatic  $CH_2$  group in ethyleneoxide)<sup>[16],[17]</sup>. The bands at 1466, 1358, 1342 e  $957\text{ cm}^{-1}$  corresponding to C-H deformation vibrations. The bands in the region at  $1146$  à  $1061\text{ cm}^{-1}$  are attributed to ether stretching vibration (C-O-C) in the crystalline phase<sup>[18]</sup>.



**Figure 2:** FTIR spectra of PEO, SWy-1 and PEO/SWy-1 (0.5%) composites.

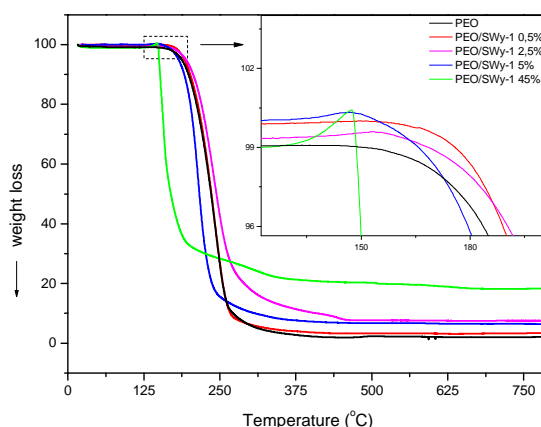
The presence of the peak at  $957\text{ cm}^{-1}$  in the FTIR spectrum, indicates that pristine PEO is in the helical conformation<sup>[19]</sup>.

### 3.2. Tests Thermoanalytical

The SWy-1 clay depicted an initial weight loss between 20 e 50 °C due to residual water. There was also a decomposition between 560 e 600 °C associated with dehydroxylation of OH groups present in the clay structure<sup>[20]</sup>.

Results of thermogravimetric analysis of pristine PEO showed weight loss between 55 e 65 °C regarding the loss of residual water. The thermal degradation of pristine PEO occurs in single step degradation and presented 2.1% of residue (0.0756 mg) at the end of the TG curve.

The Fig. 3 presents TG curves of PEO/SWy-1 composites with different amounts of clay. As well as the pristine PEO, the thermal degradation of composites occurred in single step degradation<sup>[21]</sup>. Furthermore, increasing the amount of clay SWy-1, observed an increase in the percent residue at the end of the TG curve. The clay, in this case, may impede the passage of volatile products resulting from thermal degradation.



**Figure 3:** TG curves of pristine PEO, PEO/SWy-1 composites with different amounts of clay obtained as dynamic atmosphere of are (100 mL min<sup>-1</sup>) and heating rate 10 °C min<sup>-1</sup>.

From the TG curves of pristine PEO and composites obtained if the initial temperature of thermal degradation ( $T_i$ ) (Table 2).

Amostras	$T_i$
PEO	150.7
PEO/SWy-1 0.5%	152.3
PEO/SWy-1 2.5%	143.8
PEO/SWy-1 5.0%	133.3
PEO/SWy-1 45%	127.2

**Table 2:** Initial temperature thermal degradation ( $T_i$ ) for the pristine PEO and composites

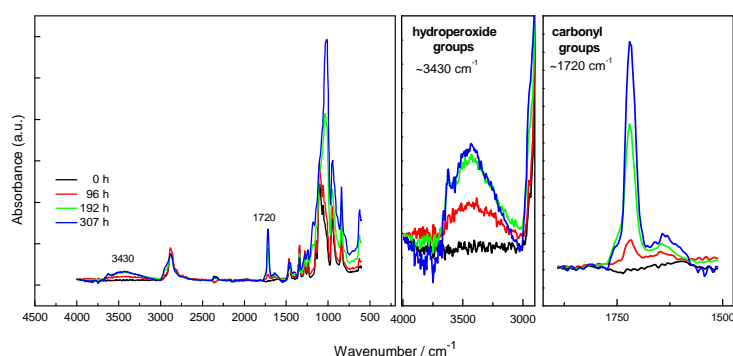
The PEO/SWy-1 composites presented  $T_i$  smaller when compared to pristine polymer (PEO), due to the possible formation of catalytically active sites that may accelerate the matrix polymeric in the presence of oxygen over thermal degradation. In the initial thermal degradation of composites with more clay, can be observed a mass gain which is more evident to PEO/SWy-1 composite with 45% of clay. This mass gain may be attributed to oxidative process which is influenced by increasing the clay.

The DSC results show a small decrease of fusion peak amplitude, located at ~64 °C with increasing quantity of clay SWy-1. These results indicate that changes occurred in the crystalline phase of PEO. In fact, the enthalpies of melting ( $\Delta H_m$ ) were calculated from the area of the DSC endothermic peak decrease from 142 J g<sup>-1</sup> (pristine PEO) to 120 J g<sup>-1</sup> (PEO/SWy-1 composites).

The proportion of PEO crystalline phase was calculated from the ratio between the melting enthalpy per gram of PEO present in the sample ( $\Delta H_m$ ) and the melting enthalpy per gram of 100% crystalline PEO ( $\Delta H_m = 196.4 \text{ J g}^{-1}$ )<sup>[22]</sup>. The presence of the SWy-1 clay in the composites has decreased the crystalline proportion, from 72% in pristine PEO, to 61% in PEO/SWy-1 composites. According to DSC results the clay hindered process polymer crystallization.

### 3.3. Photooxidative degradation of composites

The Pristine PEO and PEO/SWy-1 (0.5%, 1.0%, 2.5 and 5.0%) composites were irradiated with UV light for up to 307 h at 40 °C. The stream of photons was  $1.78 \times 10^{21}$  photons/m<sup>2</sup>s for the irradiation of the films. The stream of photons was calculated using the equation describe by Neumann *et al*<sup>[23]</sup>, and the emission light (Fig. 7) was determined using a SPR-01 spectroradiometer (Luzchem). The changes caused during UV irradiation of PEO/SWy-1 films were accompanied by FTIR and are showed in Fig. 4.

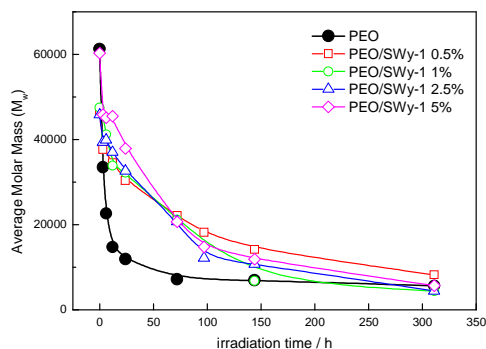


**Figure 4:** FTIR spectra of PEO/SWy-1 5% composite film as a function of irradiation time.

Can notice the formation of news bands at 1720 and 3430  $\text{cm}^{-1}$ . The increasing of the band at 1720  $\text{cm}^{-1}$  can be attributed to the formation of carbonyl species ( $\text{C}=\text{O}$ )<sup>[11],[12],[18]</sup>. The band at 3430  $\text{cm}^{-1}$  is attributed to the formations hydroxyl and hidroperoxyde groups ( $\text{OH/OOH}$ )<sup>[24]</sup>.

### 3.4. Size Exclusion chromatography (SEC)

The variations in weight average molecular weight ( $\overline{M}_w$ ) was monitored by size exclusion chromatography (SEC). The molecular weights ( $\overline{M}_w$ ) of PEO and SWy-1/PEO films are in the range of 60,000 and 50,000, respectively. Whereas the  $\overline{M}_w$  of pristine PEO was reduced to 50% of its initial value after 3 h of irradiation, the same reduction was only achieved after about 72 h for the SWy-1/PEO (Fig. 5).

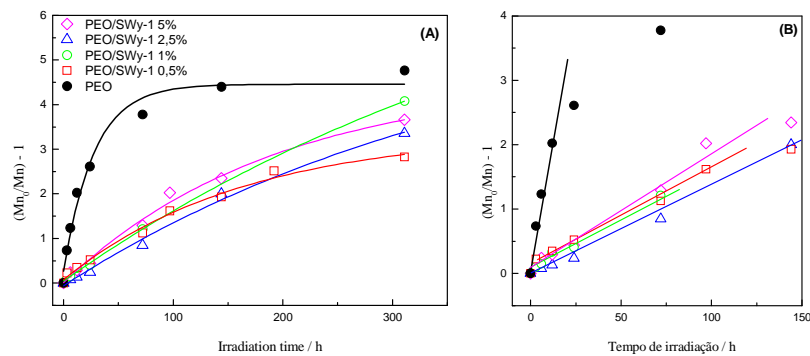


**Figure 5:** Evolution of the molecular weight ( $\overline{M}_w$ ) during photooxidative degradation of PEO and composites.

The polydispersitivity ( $\overline{M}_w/\overline{M}_n$ ) of the all samples decrease from 2.7 for 1.3 during irradiation. Besides the narrowing of the chromatographic curves for samples irradiated indicates that the polymer tends to be less disperse. Simultaneously, a new peak at longer retention time appears on the chromatographic curves during irradiation, which can be attributed to the formation of products with lower molecular weight<sup>[10]</sup>. The model for polymer degradation described by Marimuthu and Madras<sup>[25]</sup> leads to a correlation between the change of the number –average molecular weight  $\overline{M}_n$  with time and the degradation rate constant  $k_d$ .

$$\frac{\overline{M}_n(0)}{\overline{M}_n(t)} - 1 = \overline{M}_n(0)k_d t \quad (1)$$

The degradation rate coefficients,  $k_d$ , for PEO and the SWy-1/PEO films were calculated from the initial slopes of these curves (shown in Fig. 6b), using the  $\overline{M}_n$  initial for each system.



**Figure 6:** (a) Variation of  $[\overline{M}_n(0) / \overline{M}_n(t)] - 1$  vs. irradiation time for the degradation of PEO and SWy-1/PEO composites; (b) blow-up of the initial times.

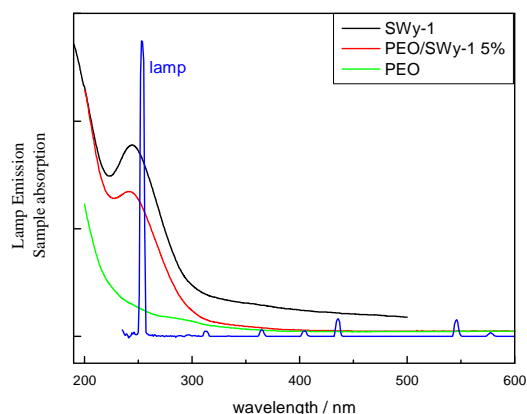
The  $k_d$  values are shown in Table 5. It can be seen that the degradation rate coefficient for pristine PEO is about 10 times larger than that for the composites.

	$\overline{M}_n(0)$	$k_d (10^{-7} \text{ mol g}^{-1} \text{ h}^{-1})$
PEO	23,200	0.700
PEO / SWy-1 0,5%	21,600	0.083
PEO / SWy-1 1%	19,400	0.073
PEO / Swy-1 2,5%	17,300	0.081
PEO / SWy-1 5%	19,400	0.077

**Table 5:** Initial number average molecular weights ( $\overline{M}_n(0)$ ) and degradation rate coefficient ( $k_d$ ) of pristine PEO and PEO/SWy-1 composites.

According to the results of the SWy-1 clay can be considered a stabilizer against UV irradiation. The stabilization mode of the clay may be explained on the ability of SWy-1, not only to scatter the incident light, but also to absorb part of the UV light thus minimizing the absorption by PEO and the degradation of the polymer in the composites. Montmorillonites characteristically shows a charge transfer transition in the 241-243 nm range which are assigned to charge transfer (oxo-Fe(III) octahedral<sup>[26]</sup>, in both films and suspensions, as can be observed in Fig. 7 Essawy *et al* observed similar effect for the photodegradation of

Laponite/PVC composites, where Laponite improved the resistance of the polymer to UV photodegradation<sup>[27]</sup>.



**Figure 7:** Emission spectra of the irradiating lamp and absorption spectra of PEO, SWy-1 and the composite film.

#### 4. CONCLUSIONS

The Poly(ethylene oxide) can be intercalated into SWy-1 via mixing in aqueous colloidal solutions to produce intercalated SWy-1/PEO composites. The TG and DSC results showed that the clay SWy-1 can accelerate the oxidative degradation of the polymeric matrix and inhibit the crystallization process of PEO. The results of photodegradation of the films accompanied by SEC showed that the rate of oxidation of PEO was faster compared to PEO/SWy-1 composites. In this case the clay can be considered as a stabilizer against UV irradiation.

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