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TOWARDS THE MICROWAVE-ASSISTED EVA ALCOHOLYSIS: A SURVEY ON HYDROGEN-BONDING AND THERMAL BEHAVIOR

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Abstract: In the present study, EVAOH terpolymer was produced by alkaline microwave-assisted alcoholysis of the ethylene-vinyl acetate copolymer (EVA). Different reaction time intervals (0.5-15 min.) were evaluated. A survey on hydrogen-bonding with alcoholysis degree and thermal behavior was evaluated. The alcoholysis degree was determined by ¹H NMR and TGA, chemical structure (hydrogen-bonding) by FTIR and thermal behavior (melt and crystallization) by DSC. The number of free carbonyls reduced linearly by the degree of reaction, showing a linear correlation between TGA and FTIR results. An unexpected increase in melting temperature by DSC was observed for polymer blends by the degree of reaction due to a positive contribution of the parameter of interaction between vinyl acetate (VA) and hydroxyls (OH) groups. The results suggested that the properties of the terpolymer are controlled by hydrogen interactions between the remaining VA and the OH groups.

Keywords: ethylene-vinyl acetate, microwave-assisted alcoholysis, hydrogen-bonding, FTIR deconvolution, thermal behavior.

Introduction

Hydrogen-bonding, dipole-dipole, and ionic interactions in polymer materials have been of great interest to fundamental polymer science and industrially, for over 40 years. These secondary or noncovalent interactions can be specifically introduced into polymeric backbone to form supramolecular materials displaying interesting thermal, mechanical, surface, and optoelectronic properties. The concept of noncovalent bonding has changed the thought of polymer scientists, who focused for many years, primarily on the effects of covalent interactions. Hydrogen bonds (H) are interactions that result from dipole-dipole forces between strongly electronegative (e.g., fluorine (F), nitrogen (N), oxygen (O)) and hydrogen atoms. There are several examples in nature demonstrating that the formation of organized structures depends on hydrogen bonds, as is the case with DNA, water, and others [1].

The partial alcoholysis of the ethylene-vinyl acetate copolymer (EVA) produces EVAOH, a terpolymer with excellent barrier properties and quite efficient in the compatibilization of polymer blends [2, 3]. This polymer system is attractive as it can be used in many applications. Therefore, the understanding of the specific interactions involving the carbonyl group is fundamental to modulate its properties. In a previous study, our group has already demonstrated that it is possible to produce more selective and less thermally degradable EVAOH copolymers through dielectric heating [4]. To date, it has not been reported the effect of alcoholysis degree on the type of hydrogen-bonding formed in the EVAOH chains. These specific interactions involve donor and

electron acceptor characteristics of the vinyl alcohol (VA) and vinyl acetate (VA) groups. Thus, two hydrogen-bonding contributions coexist in equilibrium in the copolymer, and it is clear that the degree of alcoholysis governs the predominance of one of them [4]. One of the contributions deals with the inter and intramolecular hydrogen interactions as $\text{OH}\cdots\text{OH}$ and $\text{OH}\cdots\text{O}=\text{C}$ ($3620\text{--}3060\text{ cm}^{-1}$), while the other is associated to the carbonyl ester formed with hydroxyls ($\text{OH}\cdots\text{O}=\text{C}$; $\sim 1720\text{ cm}^{-1}$). These structural peculiarities in the EVAOH copolymers cause significant changes in their physicochemical properties [3]. In this study, we are ready to establish a correlation between alcoholysis degree with hydrogen-bonding and thermal behavior.

Experimental

EVAOH copolymers were produced from microwave-assisted alcoholysis of ethylene-vinyl acetate (EVA) (Brakem Co.; 28 wt% of VA) using alkaline catalysis. The reactional procedure was described in detail by Paradinha et al. [4]. In a flat bottom flask (250 mL), 19 g of EVA pellets were dissolved in 114 g of the solvent (THF) medium at $45\text{ }^{\circ}\text{C}$. Then, a certain amount of an alcoholic NaOH solution (0.5M) was added into the reaction medium. Reactions were conducted using the magnetron (650W) operating with 4 s on and 15 s off, during different time intervals (0.5–15 min). After alkaline hydrolysis reaction, the products were neutralized with 7.5 mL of 3M HCl solution and desalted with boiling ultrapure water (Milli-Q) to remove traces of sodium acetate. The alcoholysis degree of the products was quantified by ^1H NMR and thermogravimetry (TGA).

ATR-FTIR analysis (Spectrum 400, PerkinElmer) confirmed the chemical structure of EVAOH copolymers and allowed the quantification of their relative hydrogen-bonding through the mathematical treatment of the bands at $3150\text{--}3600\text{ cm}^{-1}$ and $1700\text{--}1750\text{ cm}^{-1}$. The spectra of the samples were obtained at $4000\text{--}400\text{ cm}^{-1}$ with 32 scans and a resolution of 2 cm^{-1} . The position of the free carbonyl bands associated with hydrogen-bonding in EVA was determined through an FTIR experiment of the neat polymer swollen in octanol for seven days. The bands were deconvoluted using Gaussian functions. The correlation coefficients obtained were around 0.99.

The melt and crystallization temperatures of the samples were determined at a DSC-50 Shimadzu equipment using two cold/heating cycle (ca 10 mg, $10\text{ }^{\circ}\text{C}/\text{min}$ under nitrogen atmosphere).

Results and Discussion

In Fig. 1 is shown the FTIR spectra for octanol, pure EVA, EVA swelled in octanol, and an EVAOH-5 (representative sample, 5 min. of the reaction) at $3150\text{--}3600\text{ cm}^{-1}$ (a) and $1700\text{--}1750\text{ cm}^{-1}$ (b). The region at $3150\text{--}3600\text{ cm}^{-1}$ was deconvoluted in two parts: one due to the $\text{OH}\cdots\text{O}=\text{C}$ interaction and another due to self-associated $\text{OH}\cdots\text{OH}$, which peak position was confirmed based on the octanol spectrum. The vinyl acetate group is known to form dipole-dipole interactions. Thus, two contributions were recorded for EVA at $1700\text{--}1750\text{ cm}^{-1}$: (I) C=O free and (II) C=O associated with dipole-dipole. The C=O contribution associated with hydrogen-bonding (III) was measured through the EVA swelling assay in octanol ($\sim 55\text{ wt.}\%$). As can be seen, the carbonyl band associated with hydrogen-bonding was around 1716 cm^{-1} . The alcoholysis degree of EVAOH can also be estimated by TGA. The thermal degradation of the EVA copolymer occurred in two steps (do not showed in the present study). Firstly, the acetate side groups are eliminated from the polymer backbone in the so-called deacetylation, and secondly occurs the formation of an unsaturated polymer backbone or polyene. Therefore, by the difference of masses in the first stage of degradation, it was possible to estimate the amount of vinyl acetate not converted to vinyl alcohol during the alcoholysis, not show here. Using the FTIR, it is also possible to determine the number of vinyl acetates that have been converted by quantification of the ratio between areas III/I at the $1700\text{--}1750\text{ cm}^{-1}$ region. Fig. 2 shows the correlation between the alcoholysis degree values

obtained by TGA (first weight loss) and FTIR. An excellent linear correlation fit was obtained ($r > 0.99$).

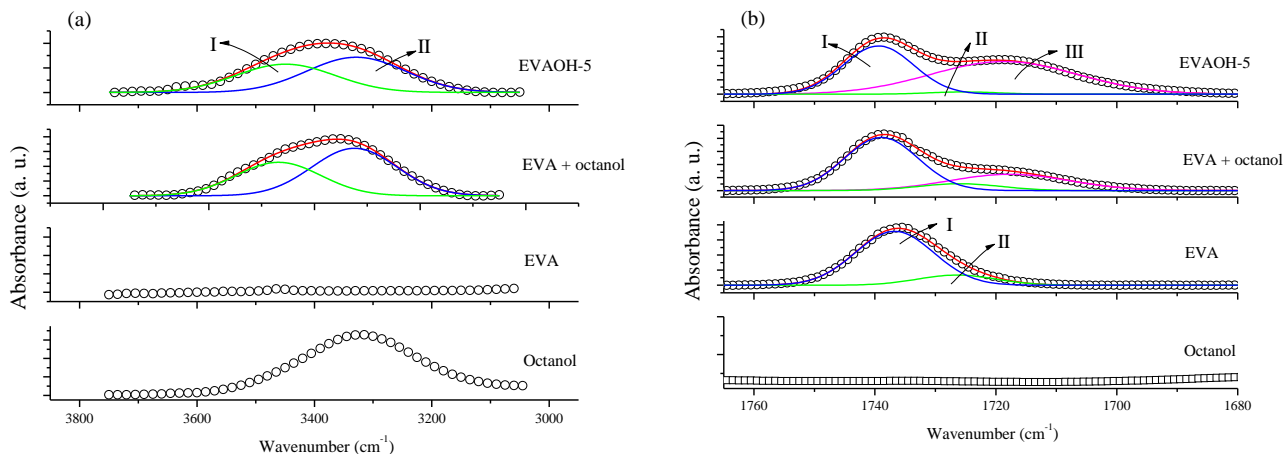


Figure 1– Peak fitting analysis: (a) in the OH region and (b) in the carbonyl region

The area of a subcomponent can be converted into the concentration when divided by its absorption coefficient. It was reported that a carbonyl group exhibits a higher absorption coefficient in the hydrogen-bonded state than at the free state. From the results, the contribution (II) in the relative dipole-dipole interaction of the vinyl acetate group becomes smaller as the degree of alcoholysis increases. Then, from Beer's law, the fraction of the free carbonyl group, Φ , can be expressed according to Eq. 1.

$$\Phi \equiv \frac{rA_I}{rA_I + A_{II} + A_{III}} \approx \frac{rA_I}{rA_I + A_{III}} \quad (1)$$

Where r represents the absorption coefficient ratio (the value used of 1.2), and A is the absorbance area.

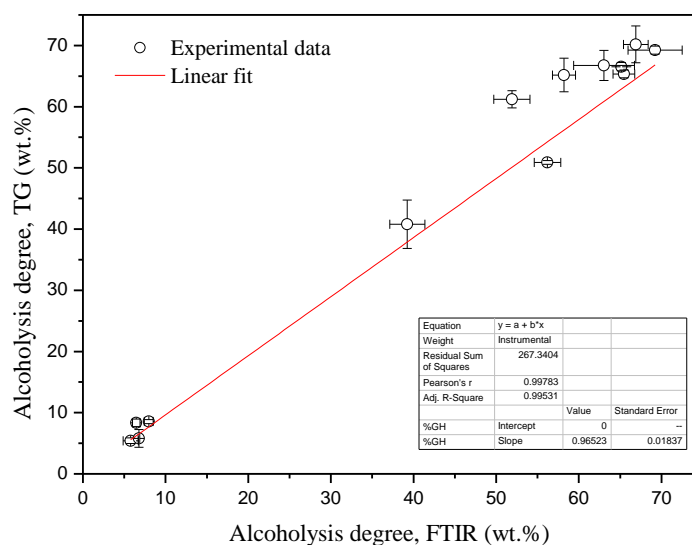


Figure 2 – Comparison between the alcoholysis degree values determined by TGA and FTIR

The amount of free carbonyls reduced linearly with the degree of reaction (Fig. 3 (a)). Thus, the hydrogen interactions between the remaining acetate group and the vinyl alcohol control the properties of the terpolymer. The hydrogen bond behavior can be related to: (1) hydrogen-bonding donor/acceptor character [5], (2) positioning of the reactive groups within the macromolecule (–OH group constitutes EVAOH backbone while the acetate group is a pendant) [6] and (3) mers sequence distribution along the copolymer chain resulting from the alcoholysis [7, 8]. Nevertheless, this behavior is undoubtedly influenced by the (4) amount and availability of -OH groups arising from the formation of VA units, which increases the probability of oxygen atoms of these groups being engaged in the H-bonding. When the amount of acetate groups in the copolymer becomes too low, they cannot correctly orient themselves to form the H-bond [9]. The structural effect of the hydrogen-bonding does not keep the relation to the dielectric heating. This, in turn, has an influence only on reaction time.

Melting temperatures (T_m) are generally depressed in crystalline polymer blends because of H-bonding, with the decrease in the value of T_m providing information about the interaction parameter and the miscibility behavior. A decrease in the T_m value provides information about the interaction parameter and the miscibility behavior. The EVA copolymer shows a reduction in its melt temperature as the amount of VA increases [4]. Nishi and Wang [10] depicted the decrease of the T_m^0 in a crystalline polymer due to the presence of an amorphous miscible component and such depression can be predicted through Eq. 2 in a simplified form:

$$T_m^0 - T_{m2}^0 = -T_m^0 \frac{BV}{\Delta H} \phi \quad (2)$$

Where T_m^0 is the equilibrium melting temperature of the pure crystalline polymer, in this case, the pure EVA; T_{m2}^0 is the equilibrium melting temperature of the EVAOH; ΔH is the heat enthalpy for a perfect crystalline polymer, B represents the interaction energy density and V is the volume fraction. In this approach ϕ represents the amount of the VA converted in vinyl alcohol (reaction degree). As shown in Fig. 3(b), an increase in melting temperature with the degree of reaction is noted. Thus, this behavior counters what is expected for polymer blends, that is, the melting temperature reduction with the increase in the number of hydrogen bonds. This is due to a positive contribution to the parameter of interaction between groups. This suggests that phase separation is occurring via the local screening mechanism.

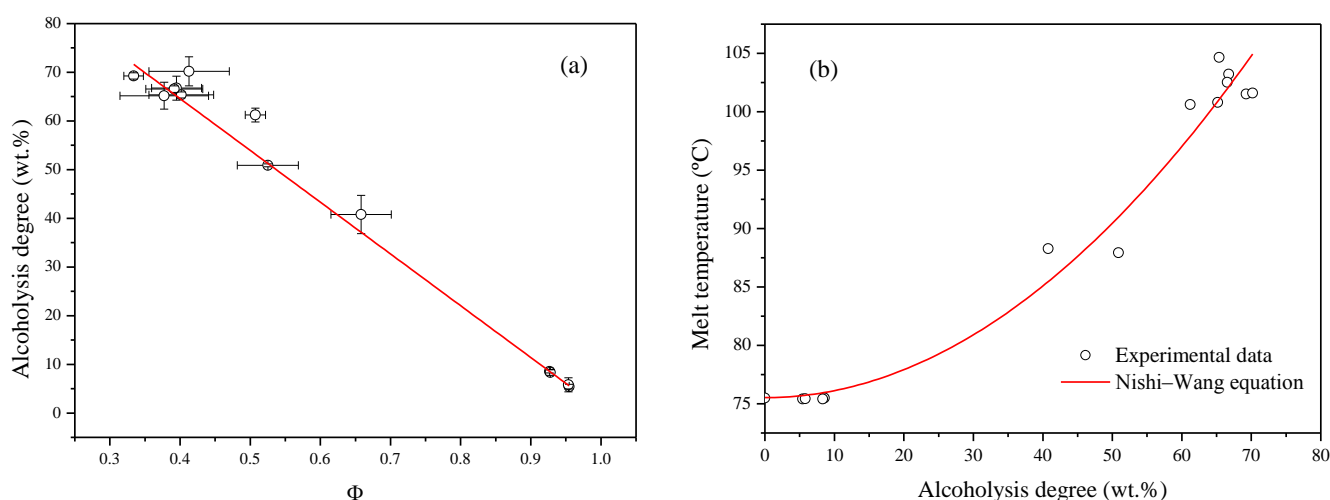


Figure 3 – Free carbonyl group vs. alcoholysis degree (a) and melting temperature vs. alcoholysis degree (b)

Conclusions

In the present study, EVAOH terpolymer were obtained from EVA via microwave-assisted alcoholysis in different reaction times (0.5-15 min.). The amount of VA not converted during alcoholysis was verified by differences in mass loss (via TGA) and using specific peak area ratios (by FTIR). A linear correlation with excellent fit was obtained between both techniques. An increase in melting temperature was verified by DSC with degree of reaction due a positive contribution of the parameter of interaction between VA and OH groups suggesting a phase separation via local screening mechanism.

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