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# The influence of moisture on the dielectric properties of poly(ethylene-co-vinyl alcohol)

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## Abstract

The influence of moisture on the dielectric properties of poly(ethylene-co-vinyl alcohol) copolymer (EVA) has been investigated using a Seiko DES 100 dielectric spectrometer between 170 and 385 K in the frequency range 10–100 kHz. A scanning rate of 1 K $\mathrm{min}^{-1}$ was used. Two peaks were observed. The $\alpha$-relaxation is ascribed to the glass transition. The presence of water facilitates molecular motion, shifting the $\alpha$-relaxation to lower temperatures. The $\beta$-relaxation is due to the local-mode relaxation in the crystalline regions of the copolymer or to the motion of hydroxyl groups. At low temperatures, water molecules may form mechanically stable bridges between the vinyl alcohol regions of the copolymer chains which inhibit molecular motion.

## INTRODUCTION

Ethylene-co-vinyl alcohol copolymer (EVA) is commonly used in diverse applications such as separation membranes, adhesives, and packaging materials [1–5]. Ethylene and vinyl alcohol monomers form co-crystals [6] in which the crystallinity depends on the copolymerization ratio [6]. In order to control the chemical and physical characteristics of EVA, chemical modification and the conditions of sample preparation have been extensively investigated [7–10]. For example, the hydrophilic properties of EVA are easily controlled by changing the copolymerization ratio [11, 12]. Molecular motion in the copolymer matrix is strongly affected by the presence of water in the system [2]. In addition, the gas permeability of EVA is dependent on the moisture content of both the copolymer and the gaseous phase [2]. However, the behaviour of EVA over a wide temperature range has not been fully investigated. The influence of a small amount of water on

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the dielectric properties of Nylon 6 [13] has been studied with a newly designed Fourier-transform dielectric spectrometer [13, 14]. In this study, the dielectric properties of EVA films are investigated over a wide range of frequencies and temperatures in the presence of a trace amount of water.

## SAMPLE PREPARATION

### *Materials*

The poly(ethylene-co-vinyl alcohol) (EVA) films used in this study were produced by simultaneously pressing (300 kg cm$^{-2}$) and melting EVA granules at temperatures higher than the melting temperature of EVA, between two sheets of Teflon. Samples with a diameter of 45 mm were cut from the films thus prepared. The granules were manufactured by Kuraray Co. Ltd. In order to investigate the effect of moisture on the dielectric properties of EVA films, one set of samples was maintained in an 81% RH environment, while a second set was stored in a dry environment over phosphorous pentoxide at room temperature. The water content of the films was measured from the weight change of the sample.

The sample preparation conditions, including pressing temperature, environmental conditioning, film thickness and water content are summarized in Table 1.

The measurements were carried out with a Seiko DES 100 dielectric spectrometer between 170 and 385 K in the frequency range 10-100 kHz. A

TABLE 1

Sample preparation and conditioning

| Sample | PE/VA ratio in mol% | Pressing temp. in K | Length of stay in envir. in days | Thickness in mm | Water content in g/g% |
|---|---|---|---|---|---|
| EVA 1 | 27/73 | 503 | Wet 133 | 0.220 | 1.15 |
| EVA 2 | 27/73 | 503 | Dry 134 | 0.198 | 0.15 |
| EVA 3 | 31.5/68.5 | 473 | Wet 137 | 0.138 | 0.50 |
| EVA 4 | 31.5/68.5 | 473 | Dry 138 | 0.141 | 0.10 |
| EVA 5 | 32/68 | 473 | Wet 139 | 0.167 | 1.89 |
| EVA 6 | 32/68 | 473 | Dry 140 | 0.198 | 0.04 |
| EVA 7 | 38/62 | 473 | Wet 141 | 0.190 | 0.86 |
| EVA 8 | 38/62 | 473 | Dry 144 | 0.167 | 0.05 |
| EVA 9 | 40/60 | 473 | Wet 145 | 0.211 | 1.05 |
| EVA 10 | 40/60 | 473 | Dry 147 | 0.174 | 0.04 |
| EVA 11 | 44/56 | 473 | Wet 148 | 0.147 | 1.85 |
| EVA 12 | 44/56 | 473 | Dry 151 | 0.162 | 0.02 |
| EVA 13 | 47/53 | 473 | Wet 153 | 0.104 | 1.10 |
| EVA 14 | 47/53 | 473 | Dry 154 | 0.155 | 0.04 |

scanning rate of 1 K $\text{min}^{-1}$ was used. An inert atmosphere was maintained using nitrogen gas flowing at a rate of 300 ml $\text{min}^{-1}$.

The samples will be referred to in the form of a ratio expressed in mol%. The first number indicates the polyethylene (PE) content; the second number is the vinyl alcohol (VA) content. Therefore, 27/73 represents a sample containing 27 mol% PE and 73 mol% VA.

The observed peaks will be denoted $\alpha$ and $\beta$ in order of decreasing temperature.

## RESULTS AND DISCUSSION

Polyethylene is an apolar molecule and gives a very small dielectric signal. The presence of hydroxyl groups in the VA chains is responsible for the observed dielectric signal in the copolymer. Disruption of the hydrogen bond network in the copolymer can also contribute to the dielectric response. Although PE is apolar, molecular motion of the PE regions of the copolymer may facilitate motion of the VA chains, leading to an enhancement of the observed dielectric relaxation. The $\alpha$-, $\beta$- and $\gamma$-relaxations of PE [15] are observed at 350, 253 K and 161 K, respectively, at a measuring frequency of 100 Hz. The $\alpha$-relaxation is ascribed to a relaxation within crystalline regions. The $\beta$-relaxation is due to main-chain motion. The $\gamma$-relaxation is ascribed to a local-mode relaxation. Dynamic mechanical analysis of PVA reveals the existence of five relaxations centred at around 455, 410, 355, 310 and 215 K [16]. The $\alpha$- and $\beta$-relaxations are ascribed to motions in the crystalline regions. The $\gamma$-relaxation is the glass transition whereas the $\delta$- and $\varepsilon$-relaxations are due to local-mode relaxation and the presence of small amounts of absorbed moisture, respectively.

Figures 1A and 1B show the storage dielectric constant $\varepsilon'$ and the loss dielectric constant $\varepsilon''$ for the 40/60 sample in the wet and dry states. In the $\varepsilon''$ curves, two peaks are clearly resolved at low frequencies (10 and 100 Hz). As the operating frequency increases, the long polymer molecules cannot respond to rapid variations in the applied electric field, which leads to observation of a single broad peak.

Due to the improved resolution of the curves at low frequencies, 10 Hz was chosen as the representative frequency in Figs. 2A and 2B to show the evolution of the loss dielectric constant ($\varepsilon''$) curves at different ethylene/vinyl alcohol contents. For clarity, only three samples are represented in these figures. At low frequencies, two peaks are observed in the $\varepsilon''$ curve for all films. The $\alpha$-relaxation is observed between 343 and 353 K when the film is dry, and in the region of 293–304 K when the film is wet. Figure 3 shows the influence of moisture on the position of the maximum of the $\varepsilon''$ peak as a function of VA content for all samples. The presence of water facilitates molecular motion, shifting the $\alpha$-relaxation peak to lower temperatures. The glass transition is reported between 338 and 346 K for EVA samples

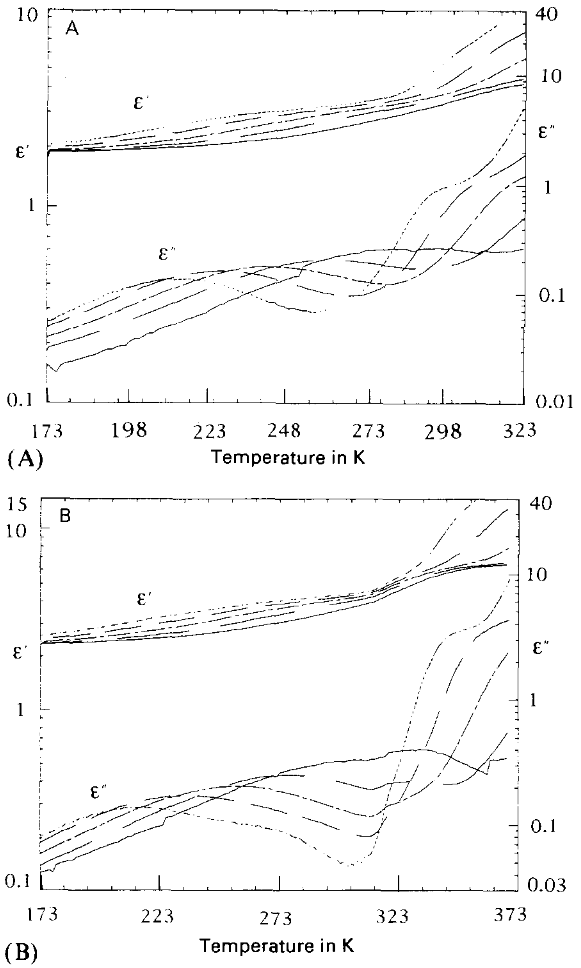

Fig. 1. A. Storage dielectric constant ε' and loss dielectric constant ε'' for the 40/60 sample in the wet state. B. Storage dielectric constant ε' and loss dielectric constant ε'' for the 40/60 sample in the dry state: ---, 10 Hz; ———, 100 Hz; ————, 1 kHz; ————, 10 kHz; ———, 100 kHz.

containing 53-73 mol% (VA) [6]. Given that the films examined in this study have similar VA contents, this peak may be ascribed to the glass transition. The peak melting temperature measured by DSC [17] and the glass transition temperature of EVA as a function of VA content are presented in Fig. 4. A broad minimum in the glass transition temperature is observed in the region of 60 mol% VA. The broad maximum in the melting temperature occurs in the region of 65 mol% VA. As the regularity of the crystalline regions increases, the melting peak temperature increases. The increase in the regularity of the crystalline regions reduces the space available for the amorphous regions of the copolymer matrix, rendering

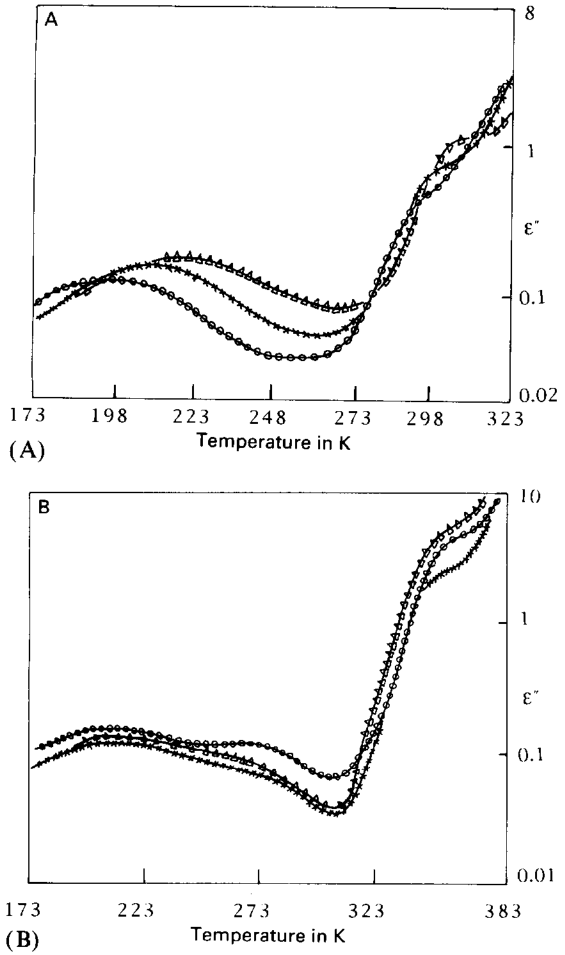

Fig. 2. A. Loss dielectric constant ε″ for the samples in the wet state. B. Loss dielectric constant ε″ for the samples in the dry state: ○, 27/73; × 38/62; △, 47/53.

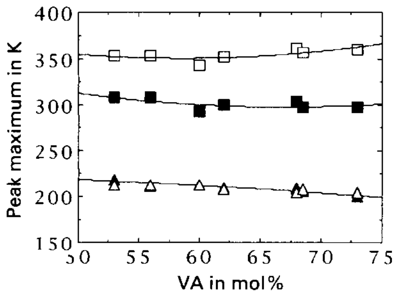

Fig. 3. Position of the peak maximum expressed in kelvins as a function of VA content: □, α-relaxation in the dry state; ■, α-relaxation in the wet state; △ β-relaxation in the dry state; ▲, β-relaxation in the wet state.

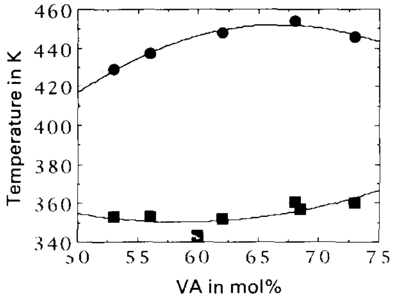

Fig. 4. DSC melting peak temperature (●) and glass transition temperature (■) of EVA in the dry state expressed in kelvins as a function of VA content.

these regions effectively more amorphous, shifting the glass transition to lower temperatures. From this, we can conclude that the EVA copolymer is not composed of separate VA and PE phases.

The $\beta$-relaxation is observed between 200 and 219 K. The position of the peak is shifted to lower temperatures as the VA content increases and, therefore, the presence of VA facilitates this relaxation. The $\beta$-relaxation, which is sometimes attributed to a local-mode relaxation, occurs at lower temperatures as the crystallinity of the sample is increased. Alternatively, this relaxation may be due to the motion of hydroxyl groups whose concentration increases with increasing VA content. The presence of water does not seem to affect the position of the maximum of the peak, as shown in Fig. 3. However, the presence of water renders the peak significantly sharper, as shown in Fig. 5 which presents the full width at half maximum (FWHM) of the $\varepsilon''$ peak of the 10 Hz signal, where $\varepsilon''$ is plotted linearly, rather than in the usual logarithmic form. FWHM is expressed in kelvin and plotted as a function of VA content in the wet and dry states. Figure 6 plots the activation energies $\Delta E$ for the $\beta$-relaxation, calculated using DES 100 software from the position of tan $\delta$ peaks in the wet and dry

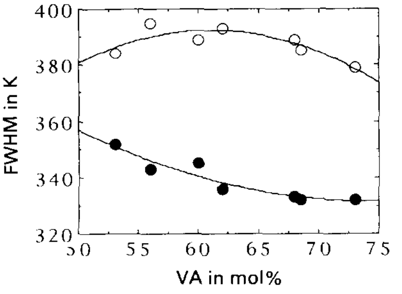

Fig. 5. Full width at half maximum of the $\beta$-relaxation peaks expressed in kelvins as a function of VA content: ○, dry state; ●, wet state.

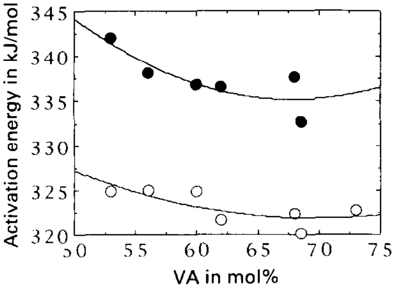

Fig. 6. Activation energy for the $\beta$-relaxation expressed in kJ mol$^{-1}$ as a function of VA content: ○, dry state; ●, wet state.

states. From this curve, it is clear that the values found for the wet state are consistently higher than those found in the dry state. Therefore, the presence of water in these systems seems to act as an anti-plasticizer, reducing the mobility of the polymer molecules. The water content of the wet samples ranges between 1% and 2%, which means that most of the water molecules are bonded to the hydroxyl groups of the VA chains. At low temperatures, these water molecules may form mechanically stable bridges between the VA regions of the copolymer chains which inhibit molecular motion.

## CONCLUSIONS

The effect of moisture on the dielectric properties of EVA has been investigated. Two peaks were observed in the low-frequency range, while only one single, broad peak is observable at higher frequencies. The $\alpha$-relaxation is ascribed to the glass transition of the copolymer and is enhanced by the presence of water which shifts the position of the peak to lower temperatures. The $\beta$-relaxation is considered to be either a local-mode relaxation occuring in the crystalline regions of the copolymer or the motion of the hydroxyl groups of the VA chains. At low temperatures, water forms mechanically stable bridges between VA regions of the copolymer chains, leading to higher activation energies in the wet state.

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