

Spectroscopic Studies of Poly(vinyl alcohol) Films Filled with a Lanthanum/*N*-Ethylmorpholine Complex

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ABSTRACT: Poly(vinyl alcohol) (PVA) films with different concentrations of lanthanum ions were prepared with a casting technique. The thickness of the prepared samples was 0.25 mm. Optical absorption and transmission measurements were performed for these samples. The ultraviolet–visible absorption spectra of pure PVA showed absorption bands at 200, 275, and 325 nm, which were assigned to the presence of carbonyl groups. The absorption spectra of doped PVA films showed an observable change in the band position with the filling levels. This was due to the link between the lanthanum metal ion and the polymer OH–groups. The dependence of the absorption coefficient on the photon energy was determined, and the band tails and energy

gaps were calculated. The band tail increased, whereas the optical gaps decreased, as the concentration of lanthanum ions increased. X-ray diffraction was used to characterize the prepared films. The results indicated the appearance of several new bands not existing for the lanthanum ions or PVA. Direct current/voltage characterization curves were measured for PVA–lanthanum films with different concentrations, and they showed remarkable increases in the conduction current of about 3 orders of magnitude in comparison with that of the pure PVA film. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1146–1151, 2007

Key words: UV–vis spectroscopy; X-ray

INTRODUCTION

The addition of lanthanides to polymeric networks is of considerable interest for both scientific and technological purposes.¹ Poly(vinyl alcohol) (PVA) is one of the most important polymeric materials because it has many applications in industry and is relatively inexpensive to manufacture.^{2–10} The optical uses of PVA include the retardation, polarization, and filtration of light, contact lenses, and drug-delivery systems.^{11–16}

On the other hand, lanthanides have many scientific and industrial uses. Their compounds are used in fluorescent lamps, lasers, magnets, phosphors, optical glass, electronics, motion pictures, projectors, and fiber optics. Lanthanide ions have unique spectroscopic characteristics, such as sharp luminescence emissions and strong paramagnetic shift properties.^{1,17,18}

PVA has been doped with different types of lanthanides ions, such as Ho⁺³, Er⁺³, Sm⁺³, and Eu⁺³,^{1,17} but until now, no spectroscopic studies on PVA films filled with a lanthanum/*N*-ethylmorpholine complex have been available.

This article discloses the effect of adding a lanthanum/*N*-ethylmorpholine complex on the optical and physical properties of PVA.

EXPERIMENTAL

La(NO₃)₃·6H₂O (10 mmol, 4.3291 g) was dissolved in 20 cm³ of distilled water and added to an equal volume of an aqueous solution containing 10 mmol (1.15 g) of *N*-ethylmorpholine. The mixture was refluxed for 2 h; after cooling, the separated white, solid complex was filtered, washed several times with ethanol, and dried *in vacuo*. The analytical characterization of the solid complex is depicted in Table I (for more details, see ref. 18).

PVA with a molecular weight of 17,000 g/mol (BDH, England) was used as a basic polymeric material in this work. The PVA films, with different amounts of the lanthanum/*N*-ethylmorpholine complex, were prepared by the casting method as follows.⁶ PVA powder was dissolved in distilled water and then maintained for 24 h at room temperature for swelling. The lanthanum/*N*-ethylmorpholine complex also was dissolved in distilled water and added to the polymeric solution. The mixture was then warmed to 60°C and stirred with a magnetic stirrer thoroughly for 4 h until the mixture was completely soluble. The solution was poured onto flat, glass plates. Homogeneous films were obtained after

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TABLE I
Microanalysis and Physical Properties of the Synthesized Complex

Complex	Color	Yield (%)	Elemental analysis ^a			
			C (%)	H (%)	N (%)	La (%)
LaL(NO ₃) ₃ · (H ₂ O) ₂	White	80	15 (15.12)	3.66 (3.57)	11.56 (11.76)	29.30 (29.18)

^a The values within parantheses are the theoretical values.

48 h of drying in an air oven at 40°C. The thickness of the produced films was 0.25 mm. PVA films filled with lanthanum/*N*-ethylmorpholine complex mass fractions of 0, 10, 20, and 40% were prepared. The lanthanum concentration [*W* (wt %)] was calculated as follows:

$$W(\text{wt } \%) = \frac{w_f}{w_p + w_f} \times 100$$

where w_p and w_f represent the weights of the lanthanum and polymer, respectively.

The films were divided into four groups (a–d) corresponding to the values of *W*. The lanthanum/*N*-ethylmorpholine complex solid was considered sample f.

The optical absorption and transmission measurements of samples a–d were measured with a Jasco V-570 spectrophotometer from 190 to 2500 nm. X-ray diffraction diagrams of the studied samples were recorded with a Philips 1430 SM diffractometer with a Cu K α target.

PVA/lanthanum samples were cut from the mother films into disk shapes with a diameter of 1 cm. The disks were coated very well on both sides with silver paint to ensure good electrical contact between the two electrodes of the sample holder. The cell used for the electrical measurements consisted of four stainless steel rods 10 cm long. Also, two stainless steel disks were used as the top and bottom bases for the four rods, along with many small ceramic parts for insulation. Very fine copper wires were cemented onto both surfaces of the holder with the paint, and each specimen was mounted on a sample holder. The direct current (A), applied voltage (V) between the two ends of the samples, and resistance (Ω) for all samples were automatically measured with a Keithley 616 digital electrometer.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of samples a–d from 190 to 800 nm. The spectrum of sample a contains three absorption bands at 200, 275, and 325 nm. The three absorption bands identify carbonyl groups of the $-(\text{CH}=\text{CH})_n-\text{C}=\text{O}-$ type (n is 1, 2, or 3), which arises from the presence of acetaldehyde in the vinyl acetate monomer during polymerization.¹⁹

For samples b and c, the spectra contain two absorption peaks at about 215 and 280 nm. The peak at 280 nm is assigned to the carbonyl groups associated with ethylene unsaturation of the $-(\text{CH}=\text{CH})_2-\text{C}=\text{O}-$ type and is indicative of the presence of conjugated double bonds of polyenes.²⁰ The disappearance of the absorption band at 325 nm indicates that the concentration of the $-(\text{CH}=\text{CH})_3-\text{C}=\text{O}-$ carbonyl group is reduced in the ligand.

For sample d, the spectrum contains only one absorption peak at about 230 nm.

There is an observable change in the band position with the filling levels (Table II). This is due to the link between the lanthanum metal ion and the polymer OH— groups. The dependence of the intensity of the bands on the filling level provides evidence for the incorporation of the complex into the PVA matrix.

Figure 2 shows the optical transmission spectra of PVA samples a–d from 190 to 2500 nm. For sample a, there is a sharp increase in the transmission intensity from 190 to 350 nm (UV region), and the transmission intensity is approximately constant (80%) from 400 to 700 nm (visible region). For sample b, the same trend can be observed, but the transmis-

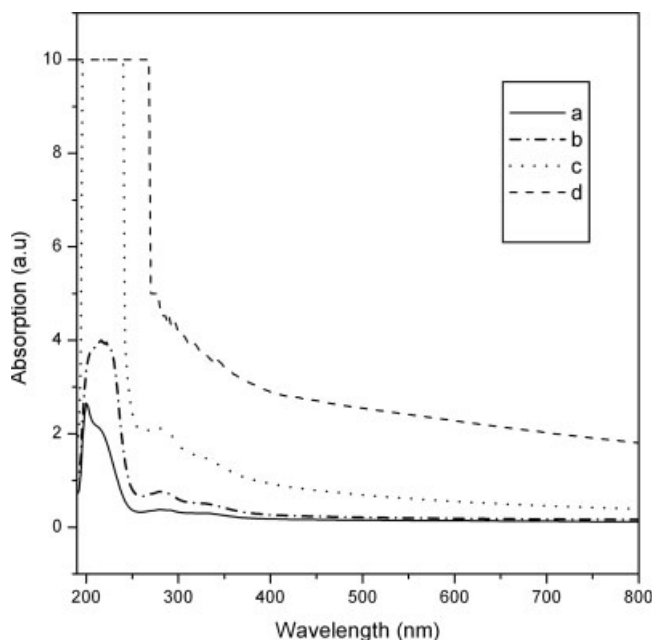


Figure 1 Optical absorption spectra of samples a–d.

TABLE II
Filling-Level Dependence of the Wavelength (λ) and Intensity of the Absorption Bands (A) Observed in Figure 1

W (wt %)	λ (nm)	A (au)
0	200	2.5
10	215	4
20	219	10
40	230	10

sion intensity decreases by 10% with respect to sample a. For sample c, the transmission intensity is zero in the UV region, and it increases sharply to 60% in the wavelength range of 300–1225 nm. With respect to sample d, the transmission intensity is zero in the ultraviolet–visible (UV–vis) region.

A general characteristic feature can be observed for samples b–d: a decrease in the transmitted light intensity occurs in the UV region from 190 to 350 nm, and a sharp decrease takes place for samples c and d that may be attributed to the strong binding of the lanthanum metal ion (present in a 1 : 2 metal–ligand ratio) incorporated into the polymer film.

Figure 3 shows the dependence of the optical absorption coefficient (α) on the photon energy for samples a–d. For all PVA samples, there is a slight increase up to approximately 455 nm (2.71 eV), which may be attributed to electronic transitions from the bonding molecular orbital to the nonbonding molecular orbital. The marked increase in α at higher energies may be attributed to an extra transition from the bonding molecular orbital to the nonbonding molecular orbital.

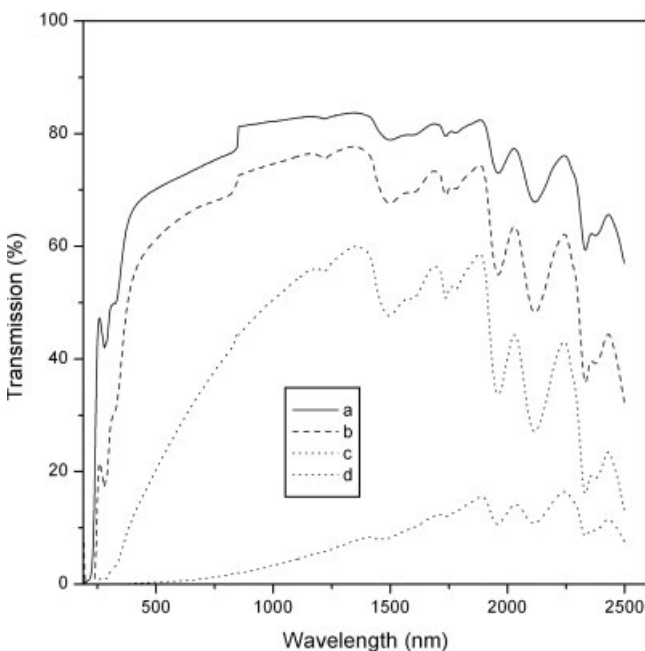


Figure 2 Transmission spectra of samples a–d.

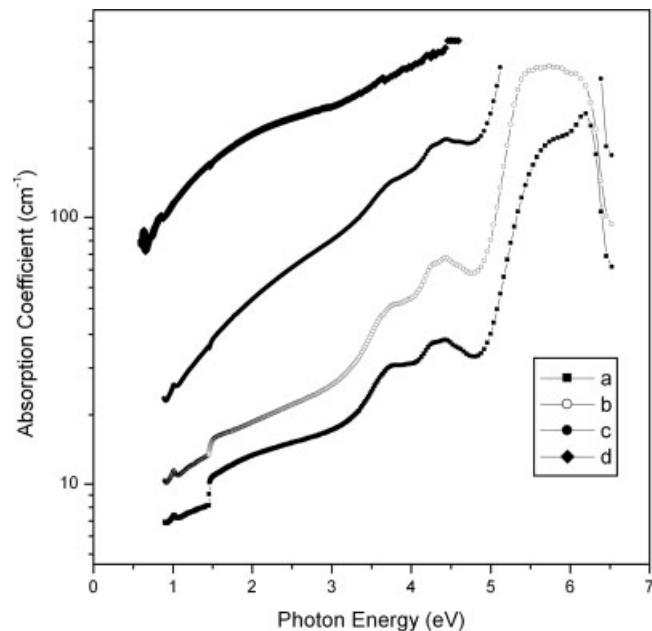


Figure 3 α versus the wavelength for samples a–d.

The absorption edge in many disordered materials follows two approaches, one given by Davis and Mott²⁰ and the other by Urbach.²¹ Davis and Mott suggested that the expression for direct transition can be written as follows:

$$\alpha(\omega) = \beta \frac{(\hbar\omega - E_{op})^n}{\hbar\omega}$$

where β is a constant, E_{op} is the optical band gap, ω is the frequency, and n is an index determined by the nature of the electronic transition during the absorption process. The most satisfactory results were obtained through the plotting of the quantity $(\alpha\hbar\omega)^{1/2}$ as a function of the photon energy, as shown in Figure 4. The values of E_{op} can be obtained by the extrapolation of the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$. Figure 5 shows the relationship between W (wt %) and E_{op} . The data can be fitted with the following equation:

$$E_{op} = 4.81 - 0.05 \times W(\text{wt } \%)$$

Urbach assumed that α near the band edge shows an exponential dependence on the photon energy and obeys the following empirical relation:

$$\alpha(\omega) = \beta \exp(\hbar\omega/E_t)$$

where E_t is the width of the band tails of the localized states in the band gap that are associated with the amorphous nature of the material. Plotting the relation between $\ln \alpha$ and the photon energy near the absorption edge produced straight lines. The reciprocal of the slope of the line was taken as the

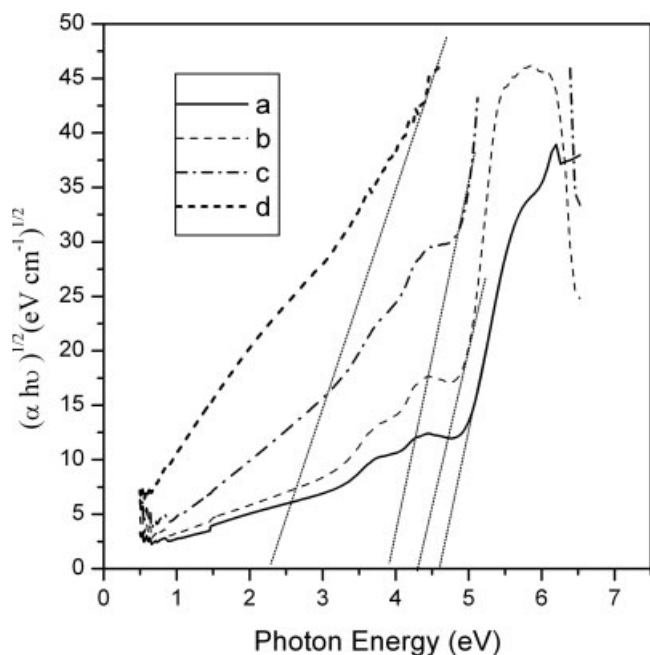


Figure 4 Dependence of $(\alpha h\nu)^{1/2}$ on the photon energy for samples a–d.

band tail of the samples. Figure 6 shows the relationship between W (wt %) and the band tail. The data can be fitted with the following relationship:

$$E_t = 0.54 + 0.005 \times W(\text{wt } \%)$$

Figure 7 shows the direct current/voltage measurements for samples a, b, and d performed under

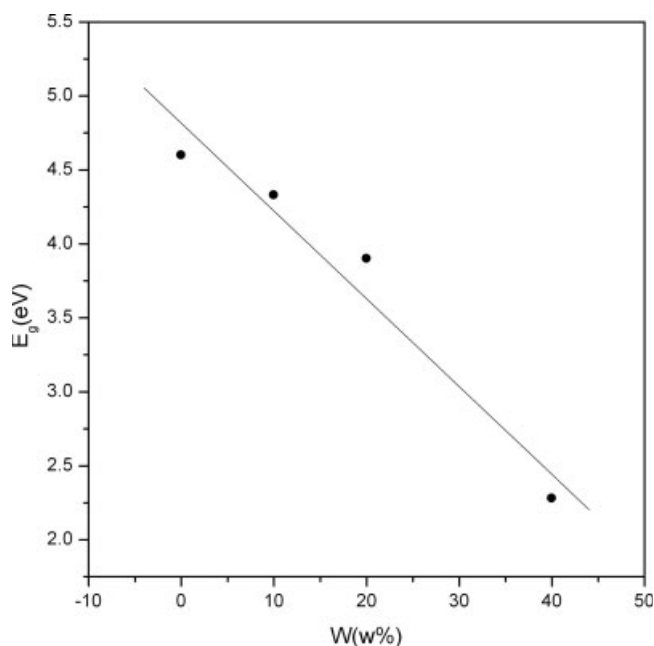


Figure 5 Dependence of the energy gap (E_g) on W for samples a–d.

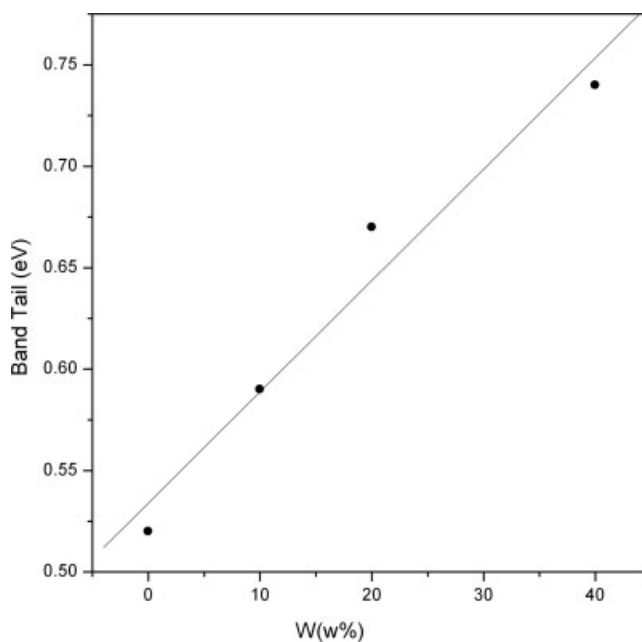


Figure 6 Dependence of the band tail on W for samples a–d.

atmospheric conditions. The current increased with increasing applied voltage. For sample d, the current increased by 3 orders of magnitude in comparison with that of sample a; this may be due to the link between the complex and the polymer moiety via lanthanum to the $-\text{OH}$ groups of the polymer.

Figure 8 displays the X-ray diffraction scans of pure PVA (sample a), the *N*-ethylmorpholine complex (sample f), and PVAs containing different levels of the *N*-ethylmorpholine complex (samples b–d). PVA, which is well known to be a partially crystal-

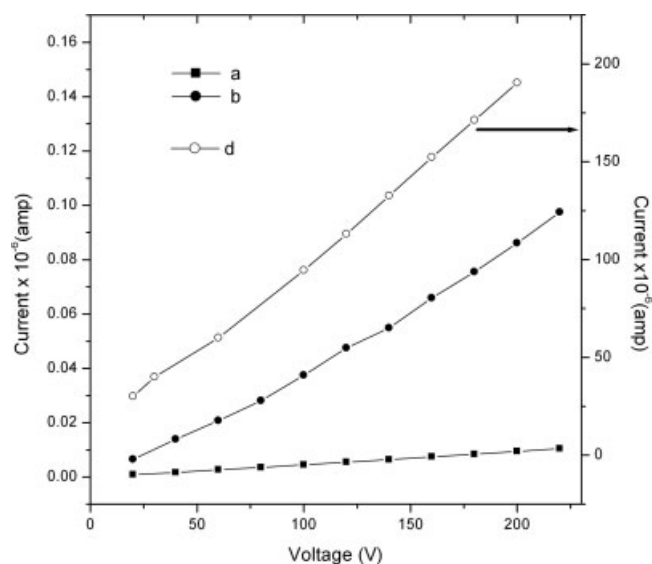


Figure 7 Direct current/voltage characteristics of samples a, b, and d.

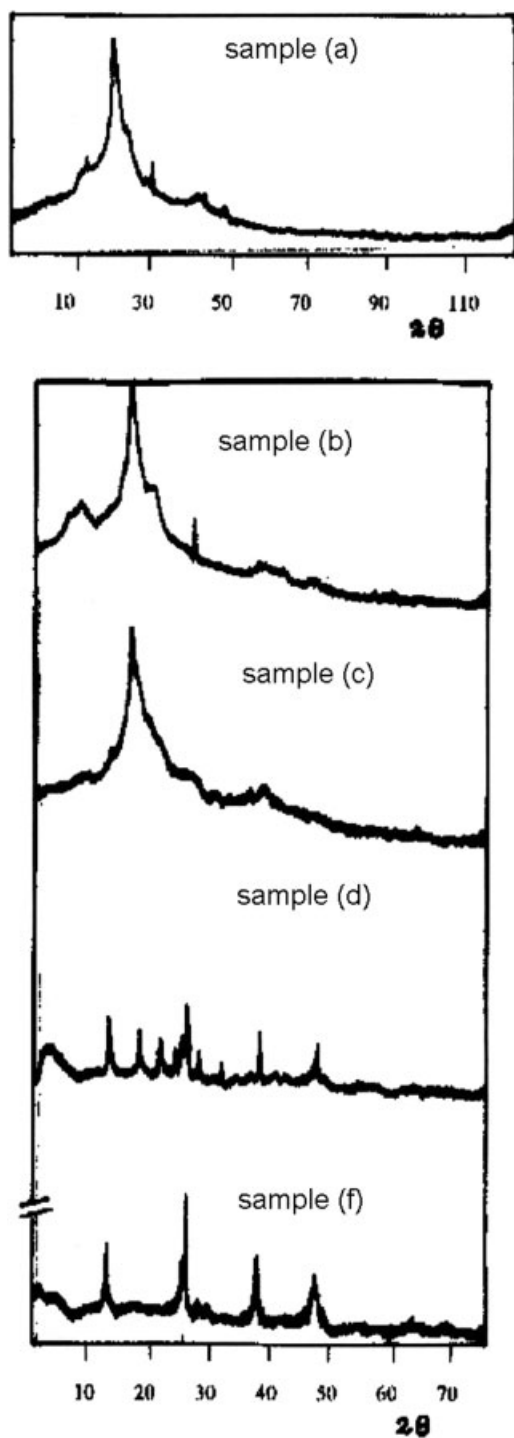


Figure 8 X-ray diffraction scans of various lanthanum filling levels for PVA films.

line polymer, shows a diffraction pattern at $2\theta = 19.75^\circ$ representing the crystalline phase,^{22,23} and this is followed by a nearby shoulder (hollow) representing the noncrystalline (amorphous) part of the sample. The crystalline nature of PVA results from the strong intermolecular interaction between the PVA chains through intermolecular hydrogen bonding. The intensity of the diffraction and also the size

of the crystals in PVA are determined by the number of PVA chains packing together.^{22,23} The *N*-ethylmorpholine complex (sample f) has five lines at 2θ values of 5, 14, 26, 38, and 48° , as shown in Figure 8; after complexation with PVA (sample b), a new small diffraction pattern appears at about $2\theta = 8^\circ$, whereas the PVA line is still at its position of 19.75° . This means that the small amount of the complex is not affected in the PVA structure. Sample c shows three diffraction patterns. The PVA line is centered at the same position, whereas there are two lines from the complex at 2θ values of approximately 26 and 38° with very weak intensity. Finally, sample d shows nine diffraction patterns: five lines belong to the *N*-ethylmorpholine complex at approximate 2θ values of 5, 14, 26, 38, and 48° , whereas four new lines appear at approximate 2θ values of 18, 22, 28, and 32° .

These experimental facts may confirm the clustering processes proposed here for PVA as the concentration of the complex increases. The disappearance of the PVA line might reflect the fact that the *N*-ethylmorpholine complex caused some kind of clustering of the PVA segments, leading to an irregular distribution of the complex in the matrix.

CONCLUSIONS

The spectroscopic investigation of the prepared polymers with UV-vis/near-infrared spectrophotometry and X-ray diffraction has been discussed. The absorption spectra of the doped PVA films show observable changes in the band position with the filling levels, and this may be due to the link between the lanthanum metal ion and the polymer OH— groups.

The energy gap and the width of the band tail have been calculated. The band tail increases, whereas the optical gaps decrease, as W is increased. Increasing the degree of disorder causes the band tail to increase, and according to the electronic structure of the amorphous materials, this will lead to a decrease in the estimated value of E_{op} .

X-ray analysis has indicated the appearance of four new lines at approximately 2θ values of 18, 22, 28, and 32° . The disappearance of the PVA line might reflect the fact that the *N*-ethylmorpholine complex caused some kind of clustering of the PVA segments, leading to an irregular distribution of the complex in the matrix.

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