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Neutron diffraction on polymer nanocomposites - A tool for structural and orientation studies

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Abstract. A series of Polyvinyl alcohol (Mowiol 5-88) – Bentonite nanocomposite films with predefined clay loading (up to 0-20%), were prepared via solvent casting technique. The developed films, due to the favourable polymer-particle interactions, revealed excellent dispersion of the clay particles in the polymer matrix and improved properties. Furthermore, the properties of PVA/clay nanocomposites as well as their structural changes as a function of the relative humidity were thoroughly investigated using neutron membrane diffraction experiments. The samples prior their measurement were equilibrated at different relative humidity levels (%RH) using either H₂O or D₂O. The application of contrast variation technique enabled us to investigate the contribution of both the polymer and the clay particles to the diffraction spectra. Thus, the use of H₂O enlightened the low Q region, providing information about the structure of the inorganic phase and specifically the stacking of the clay platelets. The diffraction patterns in this region obtained from perpendicular and in-plane sample positions revealed that there is a specific orientation of bentonite plates, parallel to the film surface. This conclusion is in agreement with the results obtained from XRD and gas permeability technique, in which the well organized and dispersed impermeable inorganic layers, increase the resistance in flow through the nanocomposites film, acting as gas barriers. On the other hand, diffraction experiments on pre-equilibrated with D₂O samples revealed the structural changes in polymeric matrix, due to hydration. The obtained peak revealed the presence of a new crystalline phase, presumably induced by the presence of the silicates, which is in agreement with DSC data reported in previous studies.

1. Introduction

Polymer-Layered Silicate Nanocomposites (PLSNs) are two-phase materials in which the polymers are reinforced by nanoscale fillers. In this type of materials, the nano-dimensioned inorganic platelets are finely dispersed in the polymer matrix offering remarkable improvement in performance properties of the polymer including high moduli [1,2,3] increased strength [4] and heat resistance [5], improved gas barriers properties [6,7], fire redundancy [8,9] etc. The control and the optimization of the above-

mentioned structural factors are expected to enable the development of nanocomposite materials with predefined superior properties.

Since the properties of the nanocomposites are defined by the dispersion of the inorganic nanoplatelets into the polymer, the degree of exfoliation /intercalation is of great importance. A number of methods have been reported in the literature for this purpose [10,11,12]. Generally, the state of dispersion and exfoliation of nanoparticles is typically studied by means of X-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) observation. Due to its easiness and availability, XRD is most commonly used to probe the nanocomposites' structure [13,14,15]. The nanostructure, namely, intercalated or exfoliated, may be identified by monitoring the position, shape, and intensity of the basal reflections, from the distributed silicate layers. For example, in an exfoliated nanocomposite, the extensive layer separation associated with the delamination of the original silicate layers in the polymer matrix results in the eventual disappearance of any coherent X-ray diffraction from the distributed silicate layers. Alternatively, for intercalated nanocomposites, the finite layer expansion associated with the polymer intercalation results in the appearance of a new basal reflection corresponding to the larger gallery height. Additionally in some cases, XRD is employed to study the kinetics of the polymer melt intercalation [16].

Although XRD offers a convenient method to determine the interlayer spacing of the silicate layers in the original layered silicates and in the intercalated nanocomposites (within 1-4 nm), little can be said about the spatial distribution of the silicate layers or the structural homogeneity of the nanocomposites. In addition, some layered silicates do not exhibit well-defined basal reflections, rendering the determination of the intensity pattern and the shape of the relative peaks difficult [17]. Therefore, in many cases conclusions concerning the mechanism of nanocomposites formation and their structure based solely on XRD patterns are only tentative.

On the other hand, TEM allows a qualitative understanding of the internal structure, spatial distribution and dispersion of the nanoparticles within the polymer matrix, and views of the defect structure through direct visualization. However, special care must be exercised to guarantee a representative cross section of the sample.

To overcome the disadvantages of the conventional techniques, numerous advanced methods have been developed for the characterization of PLSNs. Recently, small angle scattering of both X-Rays and neutrons, has been employed to characterize the nanocomposite structure and provide a measure of nanoparticle orientation [18,19,20,21,22]. Furthermore, the effect of shear on the orientation of polymer-clay nanocomposites has been examined by several groups [23,24,25]. Additionally, contrast variation or contrast matching SANS has been considered as very powerful tool for investigation of multicomponent nanocomposite systems, e.g., clay-polymer solutions [26] silica-polymer suspension [27] etc.

The aim of this work is to employ neutron membrane diffraction to study the dispersion and orientation of the clay layers in the polymeric matrix, and mainly to monitor the structural changes (crystallinity, swelling, disordering and migration of clay layers) as a function of the relative humidity of the composites. To this end, PVA/Bentonite nanocomposites with different clay loading were prepared by effective dispersion of the inorganic platelets into the PVA matrix, via solvent casting technique. The developed nanocomposites were studied by a variety of conventional techniques. Due to the favourable polymer-particle interactions, the materials exhibited excellent dispersion of the clay particles in the polymer matrix with improved mechanical strength and advanced gas barrier properties, while they retained their optical transparency even at high clay loadings (20 wt %). Furthermore, the solvent equilibrated films were studied by neutron diffraction (V1 diffractometer, HZB, Germany) using H₂O and D₂O. The diffraction patterns obtained from different sample orientations relative to the neutron beam (in-plane and perpendicular) revealed that there is a specific orientation of bentonite plates, parallel to the films' surface. This conclusion is in agreement with the results obtained from XRD and gas permeability measurements.

2. Experimental

2.1. Materials and Methods

Low viscosity, partially hydrolyzed atactic Poly(vinyl alcohol) Mowiol® 5-88 (Average weight molecular weight: 37000 g/mol - Sigma) was used for the preparation of the nanocomposites. Bentonite (cationic exchange capacity of 80 meq/100g) was supplied by S&B Industrial Minerals S.A. The purity of raw clay used in this study was about 76%.

The dispersion of the clay platelets was investigated by classical XRD and TEM techniques. The XRD patterns were recorded on a Siemens XD-500 diffractometer using CuK α 1 radiation source. Furthermore the Electron Transmission images were obtained using a Jeol JEM 2011 TEM.

The oxygen permeability experiments at 23 °C and variant %RH were performed on a PBI Dansensor OPT-5000 instrument, according to ASTM F2622-08 method. The samples, prior to their testing, were conditioned in oven at a temperature of 50 ± 2 °C for 48 h (ASTM D 618 – Procedure B).

The mechanical strength of the films was measured by means of a Thumler GmbH Tensile Tester Model (cell load 250N -PA 6110 Nordic Transducer), using specimens of 3 cm width and 6 cm length. Prior the testing, the samples were pre-equilibrated at constant relative humidity.

2.2. Preparation of PVA/Bentonite nanocomposites

A PVA solution in water (10 wt%) was produced (6 hours mixing at 90°C) and used as stock solution. The samples were prepared by mixing water suspensions of bentonite with the polymer solutions in quantities that gave 5, 10 and 20 wt% clay loading on the final films (PVAB05, PVAB10 and PVAB20, respectively). Initially, the mixture of polymer and bentonite (100ml) was stirred for half hour at 80°C and then sonicated for an extra half hour. The suspension (10 to 20 ml regarding the final film thickness) was poured in square (12x12 cm) polystyrene Petri dishes and left to dry slowly at 25°C for about 15 days. The average thickness of the samples used for permeability and mechanical tests was 0.1 ± 0.02 mm.

2.3 Neutron diffraction experiments

Neutron diffraction experiments were carried out on the V1 membrane diffractometer at the Berlin Neutron Scattering Centre of the Helmholtz Center Berlin for Materials and Energy (Berlin, Germany). V1 diffractometer is extremely well suited in this respect, not only due to its geometry but also because of the unique sample environment (in terms of controlled relative humidity) and pertinent know-how available [28,29,30,31].

Experiments were performed on pre-equilibrated with H₂O or D₂O at two different sample

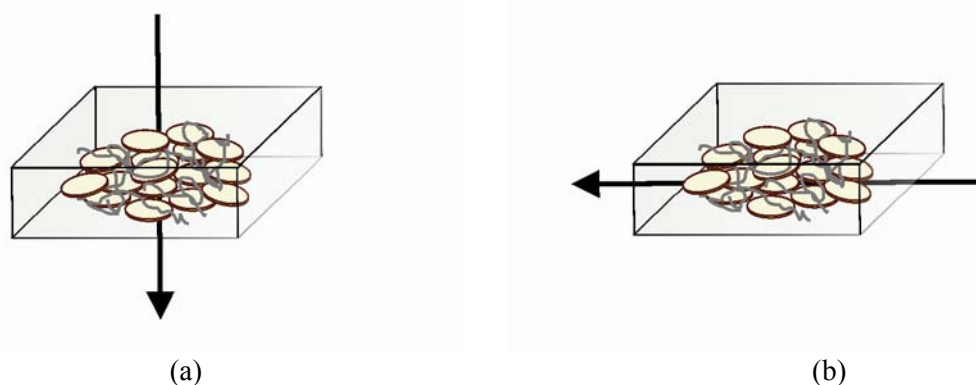


Figure 1. Experimental setup for neutron diffraction measurements: (a) perpendicular and (b) in-plane geometry

orientations, i.e. perpendicular and in-plane to neutron beam (Figure 1). To this end, film samples were placed between quartz microscope slides with the aid of a specially constructed holder. The holder was placed in a hermetically sealed aluminum can, equipped with a H₂O (or D₂O) reservoir in order to retain the equilibration conditions during diffraction measurements. The can was attached onto a goniometer head and was further connected to a circulating water bath for temperature control. Prior to the experiment the sample was aligned parallel to the beam with a laser pointer.

The diffraction patterns were obtained by rocking the sample at different fixed angles. The two-dimensional position sensitive ³He detector of V1 was set to move in steps of approximately 1-2° in 2θ, starting as close as possible to the main beam. At each detector angle (2θ), the sample was rocked through a range centered on half the detector angle (ω). The data were corrected for detector response and sample absorbance then integrated to give lamellar intensity as a function of q (Å⁻¹). The neutron wavelength and sample to-detector distance were 5.23 Å and 102.38 cm, respectively.

3. Results and discussion

3.1. Characterisation of nanocomposites using XRD and TEM

Transmission Electron Microscopy (TEM) was used to for the preliminary characterization of the nanocomposites studied in this work. Emphasis was given on the investigation of the inorganic layers' dispersion into the polymer matrix. Typical TEM images of the 20 wt % clay loaded sample (PVAB20) are shown in Figure 2.

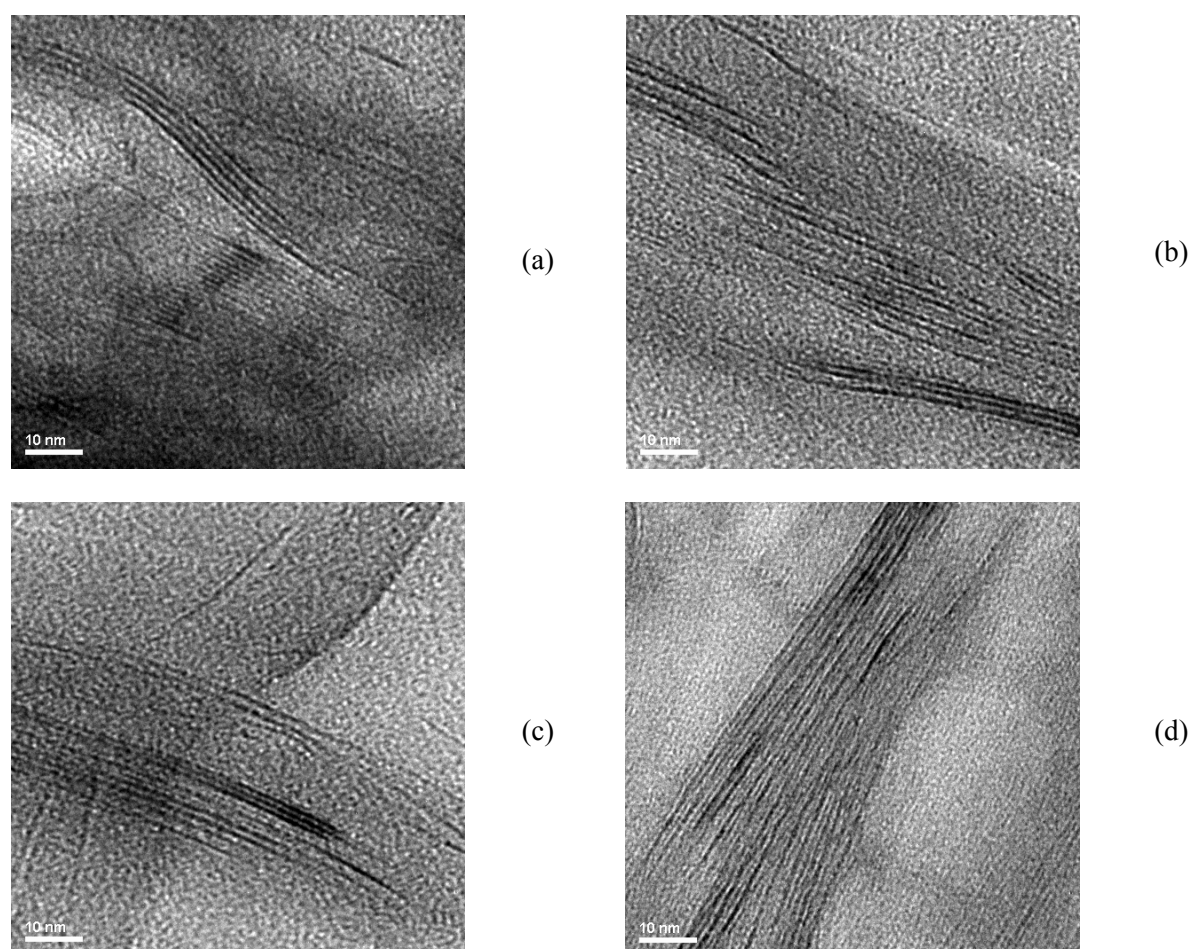


Figure 2 . TEM images of PVAB20 nanocomposites

TEM observations revealed the existence of silicate layers in the exfoliated state, while some larger intercalated tactoids could also be identified.

The XRD patterns of bentonite powder, pure PVA film and nanocomposite film (only the PVAB20 is presented for simplicity) studied in this work are shown in Figure 3. The peak at $2\theta = 19.4^\circ$, which corresponds to a dimension of $4.57 \text{ \AA}$, can be attributed to crystal reflections ($10\bar{1}$ and 101) of the polymer [32]. In the case of clay sample, the peak at $2\theta = 7^\circ$ is referred to the basal spacing ($\sim 12.6 \text{ \AA}$) of the bentonite platelets, while the other peak (around 29°) can be related to clay impurities. On the other hand, the observed increase in the basal spacing of PVAB20 sample (around $27 \text{ \AA}$) reveals the formation of intercalated structures, in which the polymeric chains were incorporated between the silicate layers resulting in a well ordered multilayer morphology. The increase in clay's basal spacing is due to favourable interactions between the clay's surface and the polymer groups. It must be noted that intercalated regions are obtained at lower clay concentration than previous studies have reported [33]. Furthermore, a small shoulder corresponding to the characteristic peak of the clay basal spacing ($2\theta = 7^\circ$) is also present in XRD pattern of PVAB20 sample, indicating that a small portion of the clay formed aggregates during the preparation of nanocomposite films.

3.2 XRD patterns in different forms

In order to investigate the potential orientation of the inorganic layers which lead to the enhanced properties of the produced nanocomposites, the XRD patterns of PVAB20 sample were measured in both film and powder forms. Initially the sample was placed on the top of the sample holder and the XRD spectra were obtained. Furthermore the sample was fragmented into small pieces and placed on the sample holder and measured again. The acquired patterns of PVAB20 sample (shown in Figure 4) reveal that the 001 peak of the clay is much more pronounced in the case of the film, giving evidence of well orientation of clay particles, parallel to the surface of the nanocomposite film.

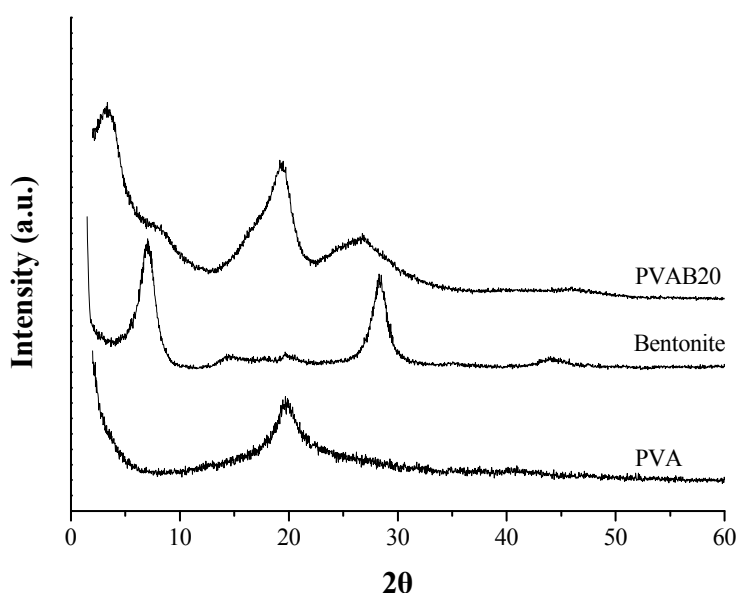


Figure 3. XRD patterns of pure clay (bentonite), PVA and PVAB20 film

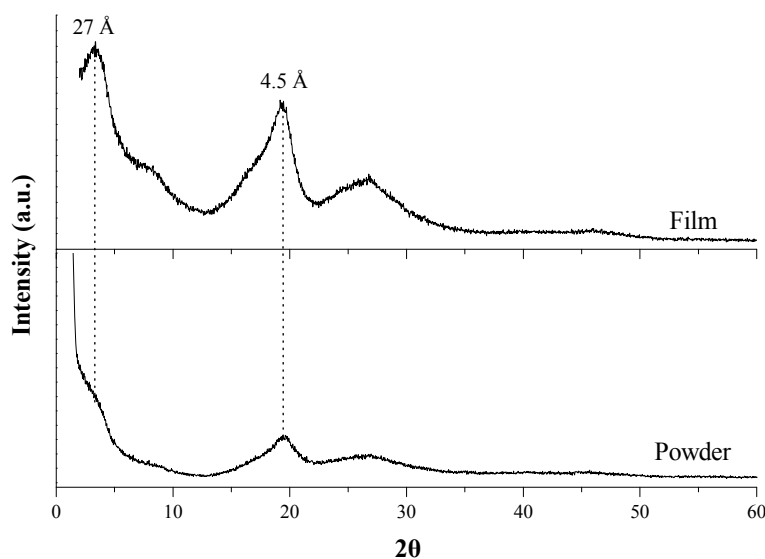


Figure 4. XRD patterns of PVAB20 sample in different forms

3.3 Properties of nanocomposites

In general, the final properties of a nanocomposite are determined by the competitive effects of polymer-polymer and polymer-clay interactions. In PVA/Bentonite nanocomposites, the polymer-clay mixing can be defined by the interactions between the functional groups of PVA and the negative charge on the clay surface. In the case of the produced films, the presence of the acetoxo groups in the selected partially hydrolised PVA together with the metal cations in the clay lattice, enabled the development of strong polymer – clay interactions. The abovementioned synergy in molecular level assisted the dispersion of the inorganic layers into the polymer matrix, leading to the formation of intercalated and exfoliated structures which enhances the overall material's performance. Therefore, the developed films, revealed improved mechanical strength, advanced gas barrier properties, increased heat resistance, while retained their optical transparency even at high clay loading (up to 20 wt %).

Figure 5 presents the oxygen permeability at 23°C at different relative humidity values in regards to the corresponding value of the neat polymer (P^{comp}/P , P^{comp} : permeability of composite, P : permeability of PVA). A significant improvement of the gas barrier properties of all samples studied is observed, due to the increased tortuosity of the permeation path which is caused by the presence of impermeable clay particles. The permeability of the PVAB5 reduced to about 50% while the corresponding value of PVAB20 (at 50% RH) decreases about 6 times in relation to that of pure PVA film. Nevertheless, this behavior is diminished at higher %RH, although the obtained permeability values of nanocomposite films are still significantly lower than of pure PVA, at the same relative humidity. This effect can be attributed to the fact that the water acts as plastisier, facilitating the transport of oxygen molecules through the film.

In general, strong polymer-clay interactions can affect crystallinity, molecular orientation, and packing of the molecules in the vicinity of the nanoplatelets, leading to an enhancement in gas barrier properties, while poor adhesion between nanoplatelets and matrix usually results in opposite effect [34,35]. In addition, the developed films exhibited increased mechanical strength (Figure 6). At ambient conditions (45 %RH), the Young's modulus of the samples increased significantly with increasing clay loading (about 260% for 20% wt clay content). The great improvement in mechanical

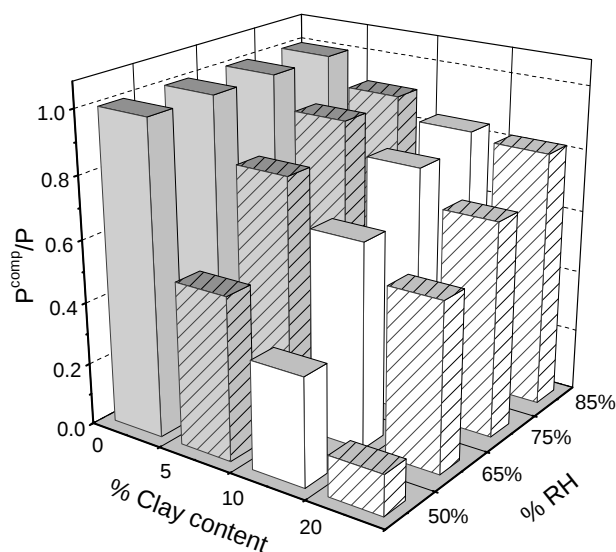


Figure 5. Oxygen permeability of PVA/Bentonite nanocomposites as well as pure PVA at 23°C

properties of the nanocomposites can be attributed to the strong interaction between matrix and silicate layers via formation of hydrogen bonds, due to the strong hydrophilicity of the clay edges [36]. Furthermore, it is clear that the effect of bentonite on the mechanical properties of the nanocomposites is more pronounced at higher %RH (increase up to 193 times for PVAB20 at 70% RH). This behavior can be attributed to the fact that, while PVA losses great percentage of its mechanical properties at

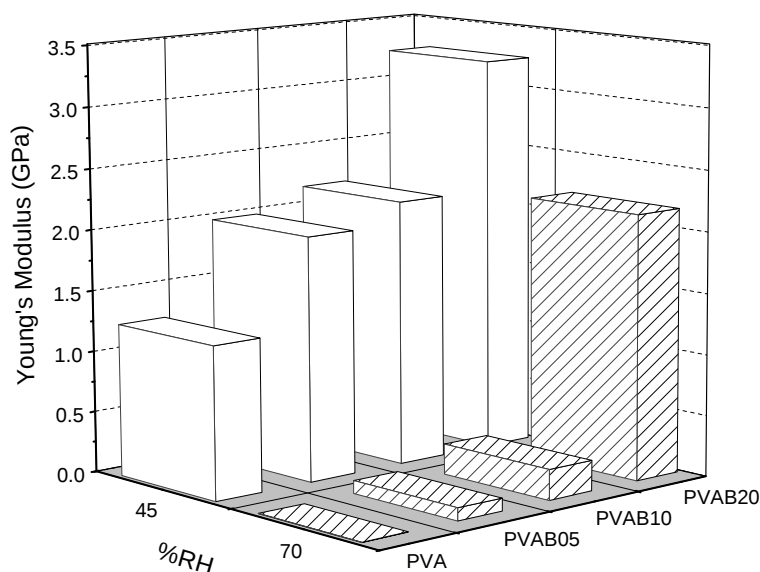


Figure 6. Mechanical properties (Young's modulus) of developed nanocomposites.

high relative humidity, clay's strength remains unaffected by water.

3.4 Neutron Diffraction

The diffraction patterns collected for PVAB20 sample equilibrated with H₂O and D₂O are illustrated in Figure 7 (a) and (b) respectively. In all samples a broad diffraction peak at around 1.39 Å⁻¹ is present, corresponding to a spacing of 4.5 Å. This peak can be attributed to the average value of the

(101) and (10 $\bar{1}$) reflections of the polymer crystals and it is typical for PVA [37,38]. On the other hand, the experimental data acquired by using the two sorbents, namely H₂O and D₂O, reveal pronounced differences especially in the range of 0.1-0.8 Å⁻¹.

Taking advantage of the different components studied, the contrast variation technique was employed to highlight scattering from the two different structural components that are present in the nanocomposite films, i.e polymer (PVA) and bentonite particles. Therefore, measurements on hydrated samples enabled us to highlight specific regions of the diffraction spectra. Due to the large differences between the scattering length density of H₂O and bentonite (Table 1), H₂O- hydrated samples were measured in order to monitor the structural changes as a function of the relative humidity of the composites at low Qregion (inorganic rich region). Thus, the shoulder at 0.16-0.17 Å⁻¹ (Figure 7a) can be related to clay structural characteristics. Alternatively, based on the higher contrast of the system D₂O/PVA (Table 1), diffraction experiments on pre-equilibrated with D₂O samples revealed the structural changes in polymeric matrix. Therefore, the obtained peak at 0.68-0.70 Å⁻¹ in the PVA/D₂O system (Figure b) can be related to polymer structure. The corresponding feature, which

Table 1. Scattering length densities of the materials used in this study

Sample	Scattering length density (Å ⁻²)
Bentonite	3.67 x 10 ⁻⁶
PVA	7.7 x 10 ⁻⁷
H ₂ O	-5.54 x 10 ⁻⁷
D ₂ O	6.34 x 10 ⁻⁶

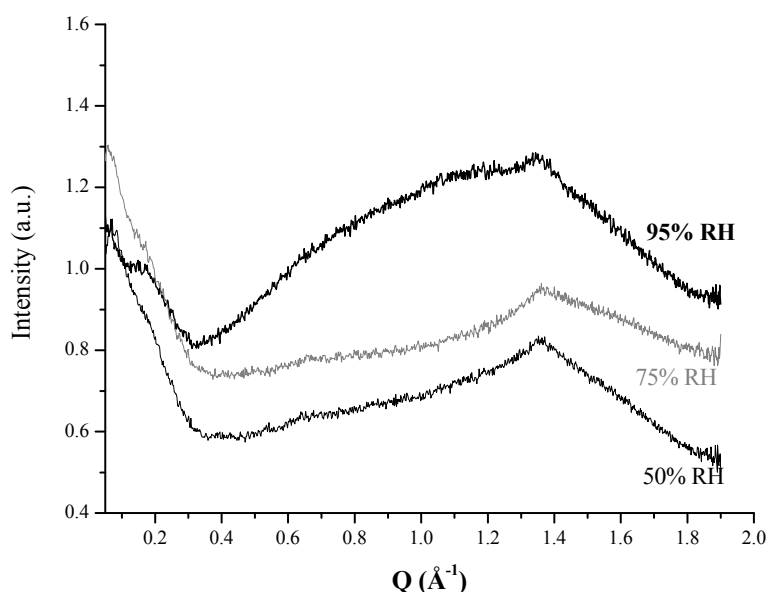


Figure 7a. Neutron diffraction patterns for PVAB20 sample pre-equilibrated with H₂O

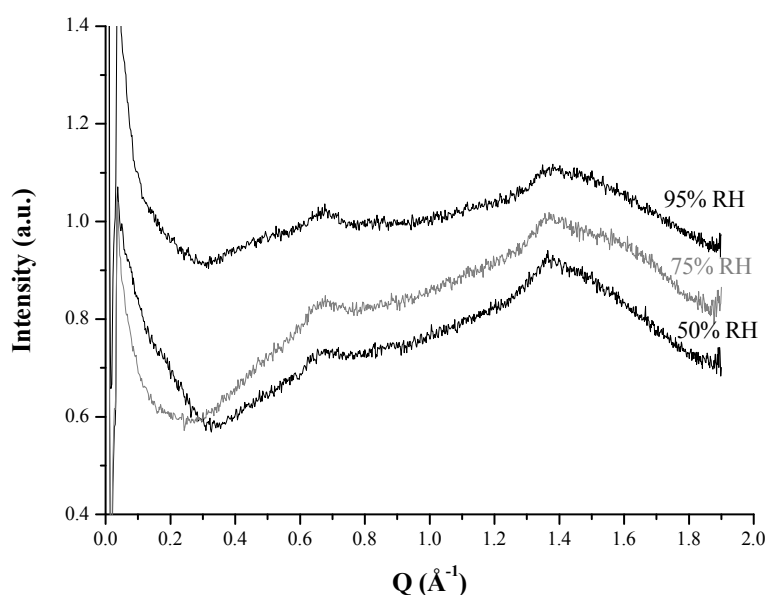


Figure 7b. Neutron diffraction patterns for PVAB20 sample pre-equilibrated with D₂O

is obvious in all %RH studied, may be attributed to the formation of a new polymeric crystalline phase, presumably induced by the silicates, during the development of the films. This assumption is in good agreement with calorimetric results (DSC) of previous studies for similar polymer-clay systems, in which the co-existence of two crystalline phases was reported [33].

Furthermore, the diffraction patterns obtained from lamellar beam incidence measurements are

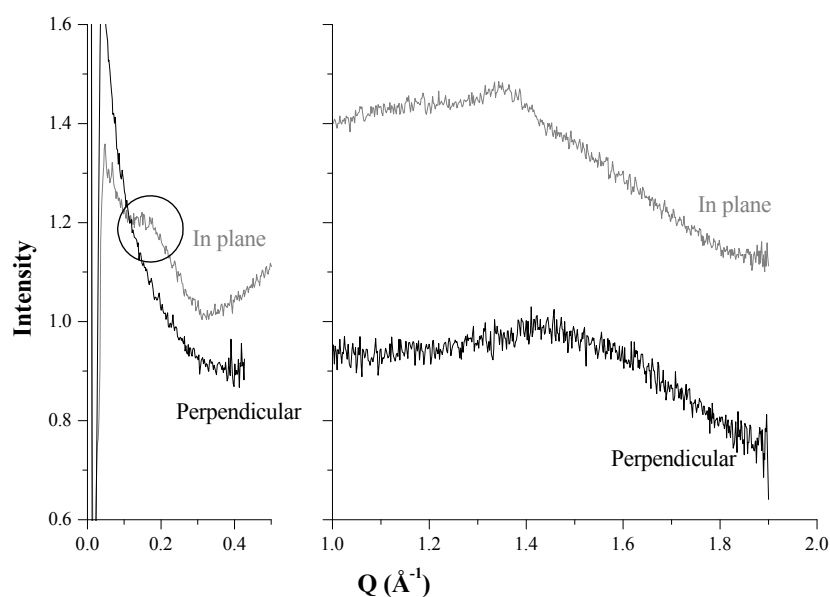


Figure 8. Perpendicular and in plane diffraction patterns for PVAB20 equilibrated at 95% H₂O.

quite different from those obtained from in-plane measurements, especially at low Q-region. In the case of lamellar measurements, a shoulder at about $0.16\text{--}0.17\text{ \AA}^{-1}$ is clearly observed. This feature can be attributed to the intercalated regions due to the effective incorporation of polymer chains between the silicate layers. Therefore, the PVAB20 sample exhibited well ordered multi-layer morphology. On the other hand this characteristic is not present in the other conformation, revealing that there is a specific orientation of the clay layers into the developed nanocomposite films, i.e. parallel to the film surface. This conclusion is in good agreement with the data obtained from XRD measurements (in powder and film form) as well as with the results derived by gas permeability technique and mechanical tests. In such a polymer-nanofiller system, oriented impermeable inorganic layers are expected to increase the resistance in flow through the nanocomposites film, acting as gas barriers.

Additionally, the excellent dispersion of the bentonite particles is anticipated to significantly boost the mechanical strength of the composites. It must be noted that the above mentioned pattern corresponds to a dimension of about $36\text{--}38\text{ \AA}$, which is notably larger than the basal spacing of $\sim 26\text{ \AA}$, determined by XRD. The observed increase in clay's basal spacing can be ascribed to the considerable swelling of the nanocomposite films due to water sorption and it has been previously reported in literature [39,40].

4. Conclusions

The properties of well characterised PVA/clay nanocomposites and their structural changes as a function of relative humidity were thoroughly studied, using neutron membrane diffraction experiments (V1 diffractometer, HZB, Berlin).

The contrast variation technique was successfully employed to investigate the contribution of both the polymer and the clay particles to the diffraction spectra. Thus, due to scattering length densities of PVA and Bentonite, measurements on H_2O -hydrated samples provided information about the structure of the inorganic platelets, in low Q-region, while D_2O -hydrated samples enabled the investigation of the structural characteristics of polymeric matrix. As a result, the obtained peak at $0.68\text{--}0.70\text{ \AA}^{-1}$ (PVA/ D_2O system) was ascribed to a new crystalline phase, which was induced by polymer–clay interactions.

Additionally, the diffraction patterns from perpendicular and in-plane geometry, in low Q region, revealed not only the dispersion of polymeric chains into the clay galleries, but also the orientation of inorganic platelets. The favourable arrangement of clay particles parallel to film surface led to nanocomposites with improved mechanical strength and advanced gas barrier properties. Therefore, neutron diffraction with contrast variation methodology can be considered as a very powerful tool for structural and orientation studies on polymer nanocomposites.

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