Abstract - Poly(vinyl alcohol)/montmorillonite (PVA/MOM) hydrogels containing coacervated microparticles of sulfonated polyester (PES) were prepared by direct mixture of the components in water. The effects of montmorillonite loading on the poly(vinyl alcohol) crystallization control were characterized by using differential scanning calorimetry (DSC) and small-angle X-ray scattering (SAXS). The influence of PES and MOM on the microstructure of the nanocomposite hydrogels was established. The intercalation of polymer chains in montmorillonite galleries markedly favors the crystallization of the poly(vinyl alcohol) matrix.

Introduction
In recent years, several research groups have studied the preparation and characterization of composite hydrogel materials. The main goal of these hydrogels is to combine the elasticity and permeability of gels with the reinforcing ability of clays embedded into the hydrogels [1-3]. Thus, the range of applications in different fields of knowledge can be extended. Montmorillonite (MOM) is the main smectite clay used to prepare composite hydrogels, due to their good water absorption, extensive swelling in water and cation exchange capacity [4-6]. The MOM structure consists of two silica tetrahedral sheets and one aluminum octahedral sheet. The layer thickness is around 1 nm, and the lateral dimensions of these layers are about 100 nm wide and long. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. These galleries are normally occupied by cations such as Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) [7,8]. These characteristics provide good interactions between clay and hydrophilic polymers in solution. Therefore, several papers have devoted attention on the features of nanocomposite hydrogels: Lee and Jou have investigated the effect of intercalated montmorillonite with (3-acrylamidopropyl) trimethylammonium chloride on the swelling and drug release behaviors of a nanocomposite constituted by N-isopropylacrylamide (NIPAAm) /acrylic acid (AA) [9]. Liu and co-authors have also observed a significant improvement of tensile properties in NIPAAm-based nanocomposite hydrogels containing modified hectorite-laponite mineral [10]. An improvement of mechanical and thermal properties was also reported by Zheng and collaborators [11] and by Lee and Lee [12] on gelatin hydrogels containing montmorillonite. Poly(vinyl alcohol) (PVA) is a water-soluble polymer, employed in practical applications because of its easy preparation, excellent chemical resistance and physical properties, and because it is completely biodegradable. Preparation and
characterization of PVA-based composites have been performed by several authors [13-16]. Our contribution with this work is to investigate the crystallization control of PVA in nanocomposite hydrogels based on PVA containing polycationic MOM. These hydrogels have an entrapped coacervated polyelectrolyte which promotes environmental-sensitivity capacity to them. The obtained results are discussed in terms of the presence of both MOM and the polyelectrolyte.

**Experimental**

*Materials and hydrogel preparation*

Natural montmorillonite (MOM) KSF \([K_{0.2}Ca_{0.3}(Fe,Al,Mg)_8(Si_4O_{10})_4(OH)_8\cdot12H_2O]\), with cationic exchange capacity of ~ 60 mEq/100g and surface area ~15 m²/g, was purchased by Acros Co. Poly(vinyl alcohol), degree of hydrolysis 99%, \(M_w 120,000\), was purchased by Sigma. Amorphous sulfonated poly(ethylene terephthalate) (PES) was supplied by Kemira, Belgium (\(M_w 60,000\)), with a sulfonation level of 20 mol %. Figure 1 shows the chemical structure of PES. All materials were used without further purification.

An appropriate amount of clay was stirred with 100mL of 0.16M CaCl₂ aqueous solution for 1h, followed by sonication during 30min. To the resulting suspension, 10 g of PVA was added and the suspension was heated under reflux for 4h with stirring. Then 10 mL of PES (2.5% wt) was carefully dropped into the suspension, resulting in coacervated PES microparticules. Table 1 shows the sample designation of the obtained hydrogels. The suspension was poured in Petri dishes and dried under vacuum until constant weight.

![Figure 1 – Chemical structure of PES](image)

*Hydrogels characterization*

Differential scanning calorimetry was performed on a DSC-7 (Perkin-Elmer). All measurements were made at a scan rate of 10°C/min, in the temperature range of 40 to 250°C, under continuous nitrogen gas flow. SAXS analyses were performed at room temperature using the beam line of the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. This beam line is equipped with an asymmetrically cut and bent silicon (111) monochromator, which yields a monochromatic...
(λ = 1.488 Å) and horizontally focused beam. A vertical position-sensitive X-ray detector and a multichannel analyzer were used to record the SAXS intensity, I(q), as a function of modulus of the scattering vector \( q = \left( \frac{4\pi}{\lambda} \right) \sin(\theta/2) \), \( \theta \) being the X-ray scattering angle. Each SAXS pattern corresponds to a data collection time of 900s.

**Results and Discussion**

Figure 2 shows the DSC curves corresponding to the pure PVA, PVA/PES and PVA/PES/MOM hydrogels. PVA exhibits an endotherm at 227°C, corresponding to the crystalline melting point (T\(_{m}\)) of PVA. The presence of the coacervated PES into the PVA matrix causes the broadening and the shifting of the melting endotherm peak of PVA to lower temperatures. These features are attributed to interactions between PVA and the coacervated PES. In fact, PVA hydroxyls are strongly bonded with PES carbonyl via hydrogen bonding. These interactions cause the disruption of the lamellar arrangement of the PVA crystallites, resulting in a diminution of average crystallite size and consequently in a lowering on the PVA melting point.

![Figure 2 – DSC curves of PVA-based composite hydrogels](image)

An interesting point is the fact that the “endothermic peak” of PVA/PES is constituted by the convolution of several peaks of small areas located at close but different melting temperature. This should indicate the existence in this system of a distribution of size for the PVA crystallites. This polydispersity is consistent with the proposed disruption of the lamellar arrangement of the PVA crystallites by adding PES. Since the crystallization degree of PVA/PES is higher than pure PVA and since the average crystallite size is lower, it indicates that the number of crystallites is higher in PVA/PES than in PVA. The DSC curves corresponding to PVA/PES/MOM hydrogels with several
MOM contents also exhibit a lower average melting temperature of crystallites compared to pure PVA. Furthermore, an increase of $T_m$ is apparent in DSC curves simultaneously with a diminution of the number of endothermic peaks compared with clay-free PVA/PES, this trend being more pronounced by increasing MOM content. This feature reveals an increase of the average size of the crystalline PVA domains and a decrease of the crystallite size dispersion by adding larger amounts of MOM in PVA/PES. In addition, it is possible to note that the addition of 1 wt% of MOM causes an increase in $\Delta H_m$ from 102 to 110 J g$^{-1}$. For higher MOM amounts the melting enthalpies decrease. This behavior can be seen in Figure 3. The degree of crystallinity of the samples were calculated from the ratio between the $\Delta H_m$ of the sample and the $\Delta H_m$ of 100% crystalline PVA ($\Delta H_m = 150.0$ J g$^{-1}$) [17]. It seems that a small amount of MOM favors the heterogeneous nucleation of the PVA chains. These nucleation effects in PVA-MOM composites were observed by Strawhecker and Manias [14], Bandi and Schirald [18] and in other semi-crystalline polymers [19]. However, increasing contents of MOM seems to induce a steric hindrance on the PVA matrix, therefore decreasing the crystallinity degree of the composites. Figure 4 shows the SAXS intensity, $I(q)$, as a function of the scattering vector, q for PVA, PVA/PES and PVA/PES/MOM hydrogels. The SAXS pattern of pure PVA shows an interference peak centered at $q = 0.06$ Å$^{-1}$, indicating an interdomain distance around 105 Å. Such feature can be explained by assuming a semi-crystalline structure of PVA. The effect of PES microparticle on the nanoscopic structure of PVA/PES is evidenced by the absence of the interference peak related to the crystalline nanodomains of PVA. As discussed below, the presence of coacervated PES leads to a new arrangement of the crystalline PVA phase inducing the formation of smaller PVA crystallites of different size. This polydispersion...
also impedes the interference effect, leading to the disappearance of the peak observed for pure PVA.

The effect of MOM incorporation on the nanostructure of the composites is evidenced by the appearance of a peak around $q = 0.33 \text{ Å}^{-1}$ in the SAXS patterns (Figure 4). The presence of this peak (001 Bragg reflection of MOM) illustrates the fact that the MOM layers retain their parallel staking, but the d-spacing (sum of the silicate layer thickness and interlayer distance) calculated from the position of the peak maximum of all PVA/MOM composites [Eq. (1)] is around 19 Å.

$$d = 2\pi / q_{\text{max}}$$

The observed increase, compared to 001 d-spacing of the pure MOM used in this work (14.3 Å, [20]), is due to the intercalation of PVA chains in the interlayer gallery. Therefore, the increase of interlayer distance for MOM in the PVA matrix is around 5 Å (considering that the thickness of the silicate layer is about 9 Å) which is an estimative of the thickness of intercalated PVA chains.

Figure 4 also shows an increase of the 001 reflection intensity by increasing MOM content. Since both the peak position and the peak width remains essentially constant by increasing clay content, this behavior is attributed to an increasing number of MOM tactoids (non-exfoliated aggregates) by adding more clay. However, this result should not be necessary associated with a larger proportion...
of tactoids by increasing MOM amounts and may be a consequence of a concentration effect. The importance of the nature of the nanostructural arrangement of MOM aggregates on the nucleating capacity to crystallize PVA chains is illustrated by comparing SAXS data with DSC measurements. As a matter of fact, a good dispersion of MOM particles presenting a plate-like morphology characteristic of a significant degree of disruption of tactoids (up to a concentration of 1% of MOM) favors the heterogeneous nucleation, thus promoting the increase in the proportion of crystalline polymer phase observed in DSC. Such nucleation effects were already observed for MOM incorporated in pure PVA, polypropylene and Nylon-6 [19,21]. For larger clay concentrations (5% and 10%) the mobility of PVA chains and consequently their ability to crystallize should be drastically affected by the formation of a three-dimensional network of linked MOM platelets in the composite, explaining the observed decrease of crystallization degree for these two samples. However, it is important to note that, despite of the existence of a MOM network at high clay contents, the process of disruption of the lamellar arrangement of the PVA crystallites by PES occurs. This is attested by DSC, SAXS and WAXS results (not shown) which indicate that the largest average crystallite size is obtained for pure PVA. The consistency between DSC and SAXS results is also illustrated by the examination of the observed increase of average size of the PVA crystallites (detected by DSC) by increasing clay amount in PVA/PES. This behavior should be explained by the larger number of PVA crystallites which should be present in the nanocomposite MOM1 compared to the samples containing more clay. As a matter of fact, a better dispersion of MOM platelets in PVA/PES and a more efficient disruption of MOM tactoids, observed in SAXS, implies in the presence of a large number of nucleating sites for the crystallization of PVA chains, limiting crystallite growth. On the contrary, a poor dispersion of MOM in the polymer matrix, associated to the existence of a three-dimensional network of linked platelets should result in a few numbers of sites, inhibiting nucleation and promoting crystallites growth.

**Conclusion**

This work shows the pronounced effect of the addition of PES and MOM on the crystallization processes of PVA polymer. It reveals that incorporation of PES promotes PVA chains mobility, decrease the PVA crystallites average size, promotes their polydispersity and finally leads to a larger degree of crystallinity than pure PVA. Except for the crystallinity degree, incorporation of MOM has exactly the opposite effect, whatever the MOM concentrations in PVA/PES. The role of the clay on the crystallinity degree of PVA is more complex: low MOM contents promote crystallization whereas a proportion of MOM larger than 5% reduces the degree of crystallinity of the nanocomposite. All of these features are related to the nanoscopic structure of the hydrogels.
which is strongly affected by adding PES and changing MOM concentrations. This study is promising aiming to control the crystallinity degree of PVA by changing clay and PES contents and the order of incorporation of PES and MOM in future preparation of PVA/PES, PVA/MOM and PVA/PES/MOM nanocomposites aiming technological applications.

Acknowledgements

We acknowledge the LNLS staff for SAXS facilities and technical support (Research proposal D11A-SAXS No. 5324/06) and Brazilian agencies CAPES, CNPQ and FAPERJ for financial support.

References

2. S. Ekici; Y. Işıkver; D. Sarayduń Polym Bull 2006; 57: 231.
10. Y. Liu ; M. Zhu ; X. Liu ; W. Zhang ; B. Sun ; Y. Chen ; H.P. Adler Polymer 2006; 47: 1.
15. Y. Yu; C. Lin; J. Yeh; W. Lin Polymer 2003; 44, 3553.