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Polyvinyl alcohol – Na montmorillonite nanocomposites films obtained by solution intercalation

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Polyvinyl alcohol (PVA) is a well known film forming polymer used in several bioapplications. His advantages related to the physico-chemical properties are induced both by a certain orientation of macromolecular chains and an advanced level of biodegradability. The main objectives of this study were the obtaining of polyvinyl alcohol nanocomposite with a natural unmodified layered silicate, the layered silicate structure investigation by XRD before and after polymer intercalation and the investigation of the thermal behavior of the PVA-NaMMT nanocomposites

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1. Introduction

Layered silicates (2:1 montmorillonite type) are inorganic species well known as clay minerals with high ordered structures. These forms correspond to tactoidal structure architectures made from individual crystalline alumino-silicates layers negatively charged (the layers structure is presented in Fig. 1). Layers structures consist in tetrahedral silica and octahedral alumina; the dimension of one layer is about 9 Å. The basal spacing of sodium montmorillonite (NaMMT) is about 12.5 Å.

The basal spacing is the distance between two bases of the tactoidal layers and the space between layers is defined as the interlayer space. The basal spacing obviously depends on the counterion dimensions. For charge compensation, alkali counterions (very often sodium) are present between layers which finally induce the tactoid formation.

One tactoid can contain from 60 to 200 layers. In water systems due high hydratation the distance between layers can be very much increased even until the dispersion of the layers (Fig. 2).

The intercalation chemistry of natural layered silicates showed a great interest in the last years due the fast development of the polymer nanocomposites. Natural layered silicates are also well known materials in the biological site in general, from swollen solution for stomach ache, up to injectable forms after a biological agent adsorption. Layered silicates can offer important barrier properties [1].

The purpose is to obtain and characterize a nanocomposite structure, by using the above presented components (Fig. 3). These hybrid materials could be used with success for pharmaceutical purposes, embolic materials, biomembranes, etc.

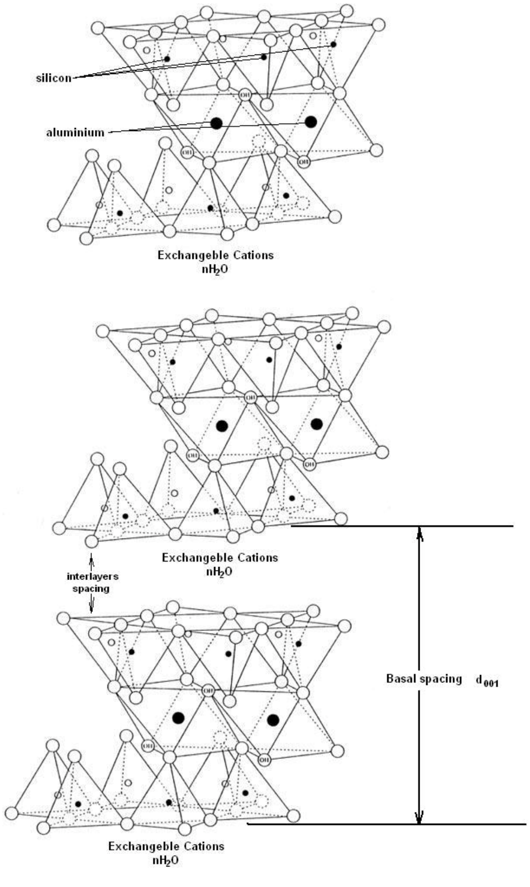

Fig. 1. Layered silicate structure (2:1 type)

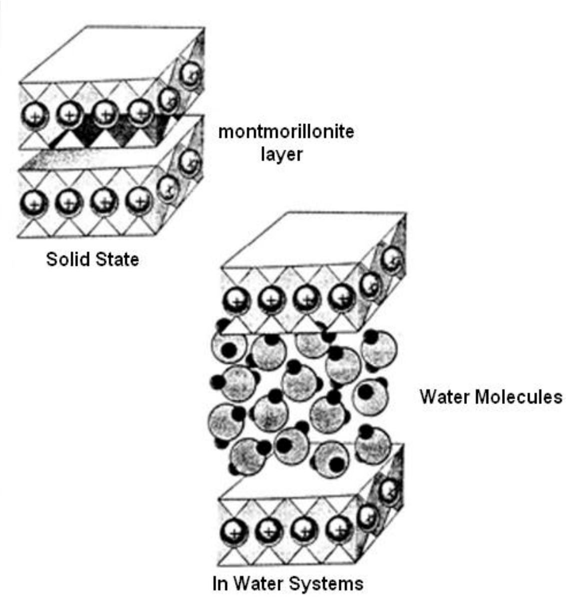

Fig. 2. The layers expansion in water systems

2. Experimental

For the hybrid obtaining was used the intercalation from solution (Fig. 4). First the inorganic filler an unmodified sodium montmorillonite (NaMMT), (Cloisite Na from Sothernclay Inc.) is dispersed in distilled water at various concentrations. The mixtures are intensively mechanically stirred over 400 rot./min. for over an hour. When a homogeneous NaMMT dispersion is achieved the PVA water solution (10%wt.) is added to the mixture under intensive magnetically stirring, but very careful not to promote the foam formation. The mixtures are stirred for over 4 hours. The dispersions are then deposed as films on polyethylene foil, and then analyzed.

The hybrid film materials were analyzed by thermal analyses (TGA-DTG) using a DUPONT 2000 instrument. The heating rate was 20^{o}C/min. A DRON-20 X-ray diffractometer with horizontal goniometer and scintillation counter was used for structure determination, by X-ray diffraction (XRD). Cu Kα (λ=1.5418 Å) radiation was filtered with Ni for the Kβ component removal, in the Bragg-Bretano (by reflexion) system. Transmition electron microscopy (TEM) was performed with a Philips CM 120.

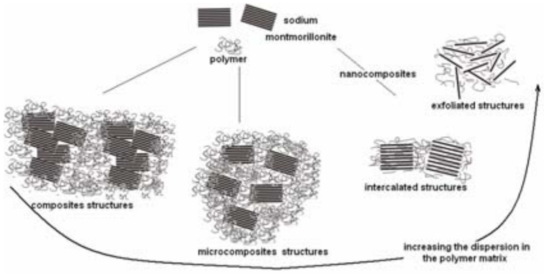

Fig. 3. Possible structures of NaMMT related on the dispersion degree in the polymer matrix.

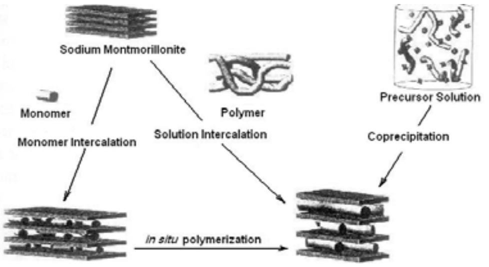

Fig. 4. Main methods for the polymer chains intercalation in NaMMT interlayer spaces.

3. Results and discussion

All the samples in water systems showed a poor stability in time, after stopping the stirring process the second day a small fraction of dense gel like phase is present on the bottom of the vials.

The films obtained on both glass and polyethylene showed were transparent at small amount of inorganic filler (0.1 g and 0.5 g of NaMMT). Only at high concentration of inorganic filler (1 g NaMMT) the film was opaque.

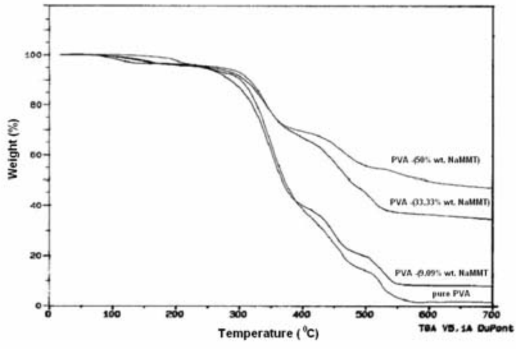

Fig. 5. TGA curves for PVA and PVA-NaMMT hybrids.

Table 1 Thermal behavior of PVA and PVA-NaMMT hybrids from DTG analyses.

Sample	PVA (g)	NaMMT (g)	H_2O (g)	TGA (^{0}C / %wt.)				
				Bonded Water	T_1max	T_2max	T_3max	Residue
APV	1	-	14	115/ 3.5	351/ 58	462/ 19.8	525/ 13	1.8
96dd	1	0.1	14	140/ 3.6	353/ 56.6	451/ 19.2	524/ 11.8	7.9
97dd	1	0.5	14	150/ 3.8	346/ 30.1	462/ 19.5	510/ 11.9	34.4
98dd	1	1	14	180/ 4.5	343/ 26.4	458/ 14.5	530/ 3.6	46.8

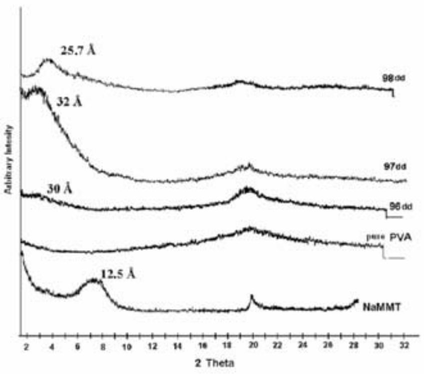

Fig. 6. XRD patterns for PVA, NaMMT and PVA-NaMMT hybrids.

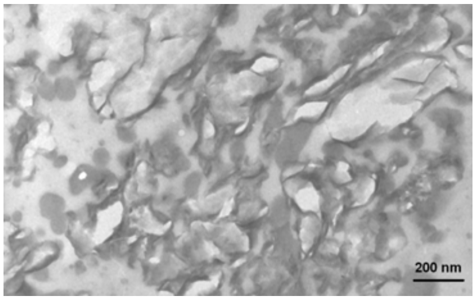

Fig. 7. TEM image the PVA-NaMMT intercalated nanocomposite.

TGA-DTG analyses showed the increase of the inorganic residue at 700 ^oC, improvement thermal stability of the hybrids and the decrease of the weight loss at 700 ^oC (Figure 5). The thermal stability of the hybrids increases on the PVA decomposition intervals only at small amounts of inorganic filler (under 5% related to the polymer matrix) (Table 1).

All the samples showed about 4 % of bonded water. The percent of bonded water does not depend on the inorganic filler load, but the desorbtion temperature of the bonded water is influenced by the NaMMT load. As the inorganic partner concentration increases the bonded water removal takes place at a higher temperature.

The XRD patterns evidenced structures which correspond to intercalated nanocomposites. The basal spacing of the layered silicate (12.5 Å) is increased in the presence of the PVA (Fig. 6). The commercial PVA showed also an orientated structure. The presence of the second peack for the NaMMT on the diffraction patterns at about 20 (θ) is due to alumino silicate layers structure.

The presence of layers in the nanocomposites structure can be seen by this peak. The fact that no peak was present at 12.5 Å demonstrates that all the NaMMT was intercalated by the PVA chains. At small load levels of NaMMT (sample 96) the diffraction peack was hardly observed corresponding more to an exfoliated structure.

TEM analyses showed the specific morphology which corresponds to intercalated nanocomposites, but small amounts of exfoliated structures could be also seen. On the TEM images the NaMMT structures show a good dispersion degree in the polymer matrix (Fig. 7).

4. Conclusions

PVA-NaMMT nanocomposites were obtained by solution intercalation.

Nanocomposites structure by XRD corresponds to intercalated nanocomposites.

The thermal behavior of the nanocomposites depends on the inorganic loads.

The best results for the thermal stability are achieved at low NaMMT loads.

The nanocomposite morphology in solid state corresponds to both intercalated and small exfoliated nanocomposites domains.

Acknowledgements

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