

Research Article

The Dependence of the XRD Morphology of Some Bionanocomposites on the Silicate Treatment

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The degree of intercalation of the polyvinyl alcohol-starch blend with the layered silicate is increased if the silicates is untreated or intercalated with ammonium ions that contain small radicals. If untreated silicate like NaMMT is used, it is possible to obtain exfoliated-intercalated nanocomposites. The materials based on PVOH, starch, and Nanocor I 28, Nanocor I 33, or Cloisite 15 A can be intercalated nanocomposites. If the blend of PVOH and starch is reinforced with Cloisite 93 A, microcomposites can result. The study will continue with the analysis of the new morphologies considering the transmission electron microscopy (TEM).

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1. INTRODUCTION

The materials obtained based on layered silicates and polymers can be of the following types: microcomposites when the polymer is not intercalated between the silicate layers, intercalated nanocomposites when the polymer chains are intercalated between the clay layers, and exfoliated nanocomposites when the clay layers are completely distributed into the polymer matrix (Figure 1). These materials can be obtained based on chemical, mechanical (melt processing), and/or chemical/mechanical methods [1, 2].

The main problems in the exfoliated polymeric nanocomposites obtaining are the silicate lamellas separation and orientation, lamellas compatibilization with the polymers, and the avoiding of the lamellas reaggregation [1–3].

The layered silicate montmorillonite (MMT) has a little affinity with the hydrophobic polymers because of its hydrophilicity. The diffusion of the polymers into the MMT galleries is possible if proper anions are intercalated within the silicate galleries. Following the stress carried out by the polymer inserted within the silicate galleries

and the mechanical shear that acts during the melt processing, it is possible to delaminate the silicate and to disperse the resulted lamellas, at nanoscale, into the polymer matrix [1, 2, 4, 5]. The performance of the subsequent silicate lamellas or tectoides dispersion and distribution within the polymer matrix will control, near the nanocomposite performances, the reproducibility of the obtained results.

The theoretical approaches of the modified layered silicate intercalation within a polymeric matrix, at the melt processing, in [1], were approached.

The nanocomposite obtaining method depends on the request of the desired application. Many applications do not require the silicate exfoliation. For this reason, before choosing the silicate exfoliation method, a careful analysis of the application performances must be done.

The morphology of the material based on the layered silicate and polymer can be appreciated also based on the XRD diffractograms (Figure 2 [1]). The *exfoliated* nanocomposites are obtained when the XRD diffractograms do not contain anymore the diffraction peak of the silicates. The *intercalated* nanocomposites are realized when the diffraction peak is

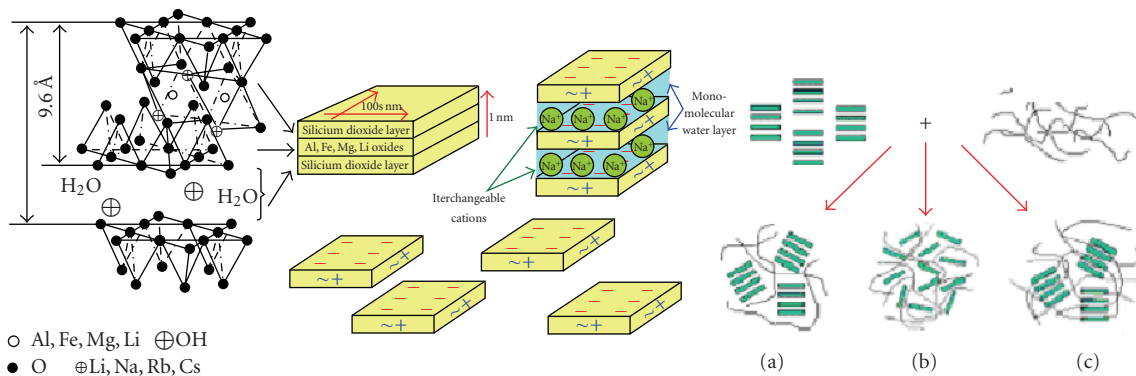


FIGURE 1: Possible nanocomposite morphologies dependent on the dispersion and distribution into the polymeric matrix of the silicate lamellas (a) microcomposites, (b) exfoliated nanocomposites, and (c) intercalated nanocomposites.

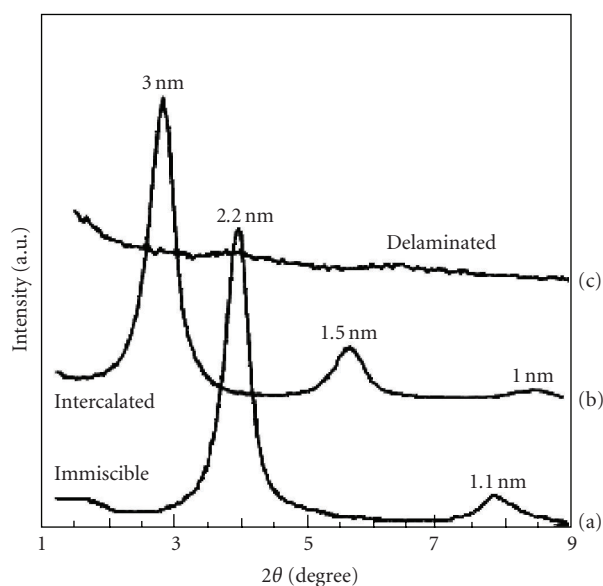


FIGURE 2: XRD diffractograms of (a) phase-separated microcomposite, (b) intercalated nanocomposites, and (c) exfoliated nanocomposites [1].

shifted toward small angles. The *microcomposites* appear in case of the immiscibility of the polymer with the silicate. In this situation, the blend peak is overlapped with those of the silicate [2].

The XRD diffractograms give also information about the morphologies of the polymer-silicate materials if the following blend diffractogram characteristics are compared with those of the silicate: number of the diffraction peaks, shifted degree of the diffraction peaks, diffraction peak intensity, and silicate galleries swelling degree.

The nanocomposites based on polyvinyl alcohol (PVOH), starch, and layered silicates are not very well studied [6–18]. These materials have a practical importance because they can be entirely destroyed in the environment as a consequence of the starch biodegradability and of the PVOH water solubility. There are known works about

the nanocomposites of PVOH with cellulose [6, 7, 17] and polyoxometalates [11]. In [8] the thermal stability of nanocomposites based on PVOH and montmorillonite (MMT) and in [9] the nanocomposites based on PVOH and bioactive glass or PVOH with chitosan and bioactive glass considering the biomedical applications are studied.

On the other hand, there are known a lot of studies concerning the materials based on starch: with poly (ϵ -caprolactone) [12], with MMT [13, 14, 18], proteins [15], and cyclodextrins [16].

The dependence of the morphology of the biodegradable materials based on polyvinyl alcohol, starch, and layered silicates by the silicate galleries treatment, in this paper, will be presented.

2. EXPERIMENTAL

The nanocomposites based on polyvinyl alcohol (PVOH), starch, and multilayered silicates were obtained by the melt processing technique [19–21]. It was studied PVOH-starch blends with the 1/1 blending ratio and 1–5% silicate loading level. The blend composition respects the rules proper to the polymeric blends through the melt processing techniques.

2.1. Materials

The following materials were used:

- (i) polyvinyl alcohol with 99 moles% hydrolysis degree;
- (ii) native starch from corn;
- (iii) silicates: treated and untreated montmorillonite (MMT) (Table 1);
- (iv) melt processing additives (plasticizers, stabilizers);
- (v) “entanglement” compatibility agents (polar compounds with small molecular weight).

2.2. Characterization

The new blend morphology was studied based on and X-ray diffraction. On a DRON 2, 0 X-ray diffractometer, the variation, at the room temperature, of the radial diffraction

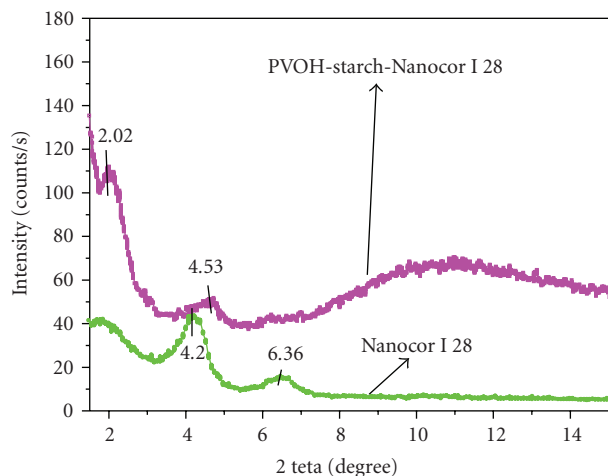


FIGURE 3: The XRD diffractograms of Nanocor I 28 and of the PVOH-starch blend with 4% Nanocor I 28.

intensity dependence on the diffraction angle (2θ) was recorded. The working conditions were: step size by 0.03° (2θ), scanning rate = 8 s/step, filter with $\lambda = 1.7921 \text{ \AA}$, and diffraction range $2\text{--}15^\circ$ (2θ). The interbasal spacing was calculated based on the Bragg law ($n\lambda = 2d \sin \theta$, where n is an integer; λ is the wavelength of X-ray; d is the spacing between the planes in the atomic lattice; and θ is the angle between the incident ray and the scattering planes).

3. RESULTS AND DISCUSSIONS

Nanocor I 28 is a layered silicate modified with trimethyl-dodecyl-ammonium ions. It has an inhomogeneous structure because its galleries do not have the same size (Figure 3— 16.1 \AA for that from 1.76° , 24.4 \AA for that from 4.2° , and 58 \AA for the diffraction from 6.36°). The main diffraction peak is that from 4.2° which has an intensity of 30 counts/s.

The shape of the diffractogram of the blend based on PVOH, starch, and 3% Nanocor I 28 is different from that of the silicate alone because the diffraction peaks are shifted toward small angles (2.02° ; 4.53°) and have different intensities (120 and 50 counts/s). The resulted morphology is more homogeneous because the silicate galleries have relatively the same size (43.7 \AA for the main diffraction peak from 2.02°). The peak intensity is 110 counts/s. All the studied PVOH-starch blends with 1–5% Nanocor I 28 have a basal spacing enlarged with approximately 20 \AA (Table 2, Figure 4). These results illustrate an interaction degree between the hydroxylic oxygen from the two polymers and the ammonium ions from the silicate galleries. The electrostatic forces, on the one hand, and the mechanical shear that acts during the melt processing, on the other hand, interpose the polymer with the silicate and enlarge the silicate galleries with approximately the same values. Because the diffraction peak of the blend is smaller than that of the silicate alone, it can be supposed that the order degree of the resulted

blend morphology is smaller. Because the diffraction peak is shifted toward small angles, the resulted materials can be an intercalated nanocomposite.

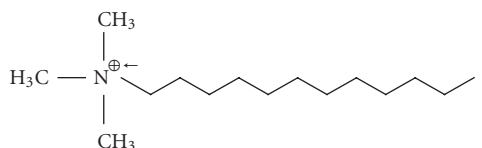
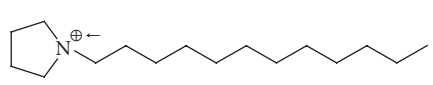
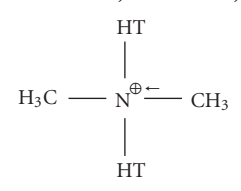
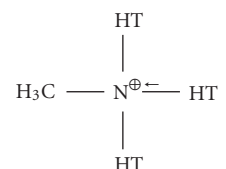
Nanocor I 33 is modified with dodecylpyrrolidone ions and has also an inhomogeneous morphology because it contains galleries of different sizes (Figure 5— $30,6 \text{ \AA}$ for that from 10.8° , $30,29 \text{ \AA}$ for that from 6.64° , and $30,23 \text{ \AA}$ for the diffraction from 3.35°). The main diffraction peak is at 3.35° and has an intensity by approximately 170 counts/s.

The diffractogram of the blend of PVOH and starch with 4% Nanocor I 33 has two diffraction peaks by smaller intensity, both of them shifted toward small angles (Figure 5—50 counts/s of the peak from 5.13° , and approximately 120 counts/s of those from 2.5°). The smaller diffraction peak can be a sign that the morphological order of the resulted blend is lower. The silicate interbasal spacing has the same size as that of the silicate. These results proved that the electrostatic interactions between the hydroxylic oxygen from PVOH, starch, and the dodecyl pyrrolidone ions from the silicate galleries are by small intensity. Because the diffraction peak is shifted toward small angles, it seems that the resulted materials can be an intercalated nanocomposite.

The Cloisite 93 A galleries contain the ammonium ions, each of them with a methyl and three hydrogenated tallow radicals ($\sim 65\%$ C18; $\sim 30\%$ C16; $\sim 5\%$ C14) [10]. This silicate has a rather inhomogeneous morphological structure because it contains galleries of different sizes (Figure 6— 13 \AA for the diffraction from 7.9° , $25, 3 \text{ \AA}$ for that from 4.86° , and 57.6 \AA for that from 1.78°). The main diffraction peak is that from 4.86° which has an intensity by approximately 110 counts/s. The blend of 4% Cloisite 93 with PVOH and starch seems to have a relatively more homogenous morphology because it shows only two peaks, one at 4.05° and a large one at approximately 5° . Because the blend diffraction and that of the silicate too take place at approximately the same angle, the diffraction peaks intensity is the same and the galleries are enlarged only with 5 \AA , it seems that there is no compatibility between PVOH, starch, and the Cloisite 93 A. This means that between the hydroxyl groups from the two polymers and the ammonium ions substituted with three radicals HT and a methyl one from the galleries no attractions are settled up. Because the blend diffraction peak is overlapped with those of the silicate, the resulted material can be a microcomposites.

Cloisite 15 A is modified with ammonium ions that contain two methyl and two hydrogenated tallow radicals. This silicate has also an inhomogeneous structure because it contains galleries of different sizes (Figure 7— $8,24 \text{ \AA}$ for the diffraction from 3.41° and $12,5 \text{ \AA}$ for that from 8.24°). If the diffraction maximum from 8.24° has a low intensity by approximately 30 counts/s, those from the 3.21° are by 95 counts/s. The blend diffractogram is totally different from that of the silicate and contains two peaks, one at 4.5° by approximately 65 counts/s and the other at 2.32° with a high intensity by 150 counts/s. The blend interbasal spacings are by $38,1 \text{ \AA}$ and 10 \AA .

TABLE 1: The used layered silicates.

Silicate (commercial grade)	Chemical formulae	2 teta (deg)	Interbasal spacing ^x , Å
NaMMT	$\text{NaAl}_{2-y}\text{Mg}_y(\text{Si})\text{O}_{10}(\text{OH})_2n\text{H}_2\text{O}$	3,45; 6,79	25,6; 12,7
Bentonita	$\text{M}_x\text{Al}_{4-x}\text{Mg}_x\text{Si}_8\text{O}_{20}(\text{OH})_4$	8,26	12,43
	Trimethyldecadecylammonium		
Nanocor I 28 [22]		1,76; 4,2; 6,36	58; 24,4 ; 16,1
	Dodecyl pyrrolidone		
Nanocor I 33 [22]		3,35; 6,64; 10,8	30,6; 30,29 ; 30,23
	Dymethyl, 2-ethylhexyl (hydrogenated tallowalkyl) ammonium		
	Hydrogenated tallow: ; ~65% C18; ~30% C16; ~5% C14		
Cloisite 15 A [23]	 HT = Hydrogenated tallow	3,21; 31,9	8,24; 12,5
	$\text{CH}_3\text{N}^+(\text{HT})_2\text{H}$		
	Hydrogenated tallow: 65% C; ~30% C16; ~5% C14		
	Anion: HSO_4^-		
Cloisite 93 A [23]	 Methyl dihydrogenated tallow ternary ammonium	1,78; 4,05; 7,9	57,6; 25,3 ; 13

^xOwn measurements.

TABLE 2: The diffraction angles and the interbasal spacing of the PVOH-starch blends with (1–5)% Nanocor I 28.

PVOH/starch/Nanocor I 28	2 teta	d, Å
1%	4,20	21
2%	2,2 ; 4,42	40,1 ; 20
3%	2,13 ; 2; 4,32	41,4 ; 41 ; 20,5
4%	2,16 ; 4,36	40,9 ; 20,6
5%	2,08 ; 4,30	42,4 ; 20,6

The possible interactions between the two polymers and the ions from the silicate galleries enlarge the galleries by approximately 9 Å. These results can be a sign that the settled interactions between the silicate and the two polymers

are of low intensity. The order degree of the resulted materials is higher because the blend diffraction peak is higher than that of the silicate. Since the diffraction peaks of the blends are shifted toward small diffraction angles, it is possible that the obtained material can be an intercalated nanocomposite.

Bentonite has an interbasal spacing by 12.42 Å (diffraction peak at 5.56°). The PVOH-starch blend with 4% bentonite has galleries by 20,3 Å (diffraction peak at 5,13°) (Figure 8). Because the diffraction peak of the obtained material is shifted toward small angle, it is possible to exist a degree of intercalation between the PVOH, starch, and the bentonite that determines a bentonite swelling degree by 7,88 Å. For this reason, it is possible that the resulted material can be intercalated nanocomposite.

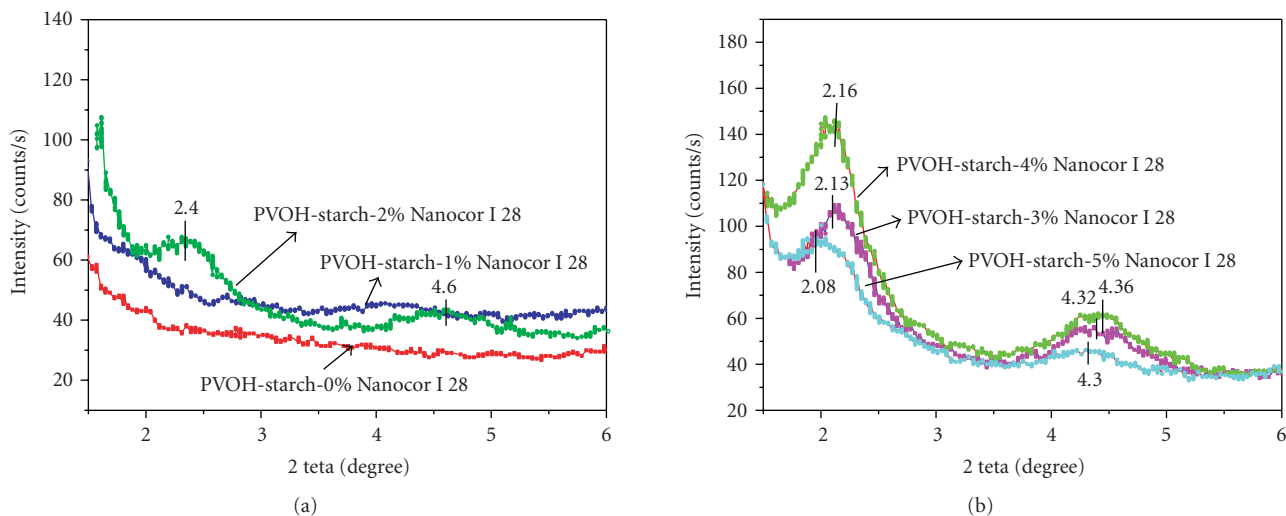


FIGURE 4: The XRD diffractograms of the PVOH-starch blends with (1–4)% Nanocor I 28 ((a) 1, 2%; (b) 3, 4%).

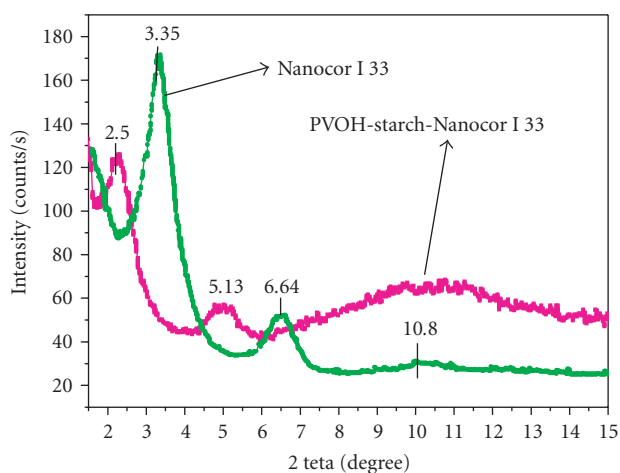


FIGURE 5: The XRD diffractogram of Nanocor I 33 and of the PVOH-starch blend with 4% Nanocor I 33.

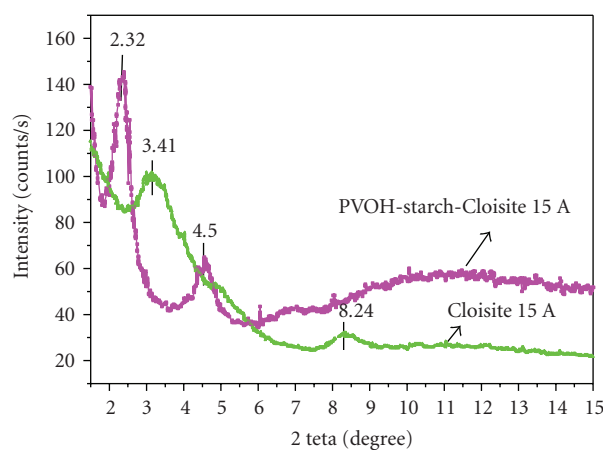


FIGURE 7: The XRD diffractogram of Cloisite 15 A and of the PVOH-starch-4% Cloisite 15 A blend.

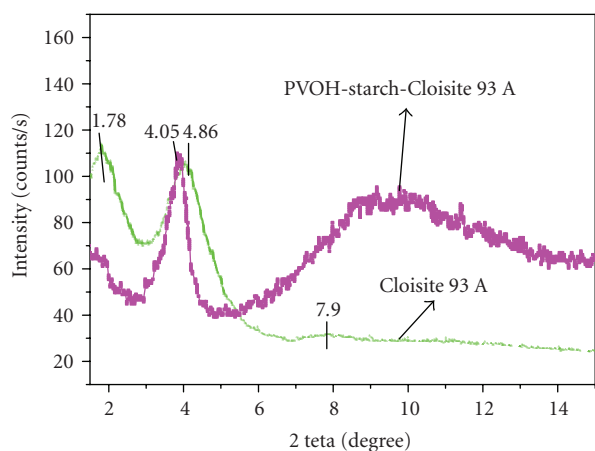


FIGURE 6: The XRD diffractograms of Cloisite 93 A and of the PVOH-starch blend with 4% Cloisite 93 A.

Natrium montmorillonite has an inhomogeneous morphology because it contains galleries of different sizes (Figure 9—25,6 Å for the diffraction from 2,93° and 12,43 Å for that from 6,85°). The XRD diffractogram of the blend of PVOH and starch with NaMMT has totally another shape than that of the silicate alone. On the blend diffractogram, only a very small diffraction peak appears at 4.92° that means a gallery by 18 Å. The silicate galleries enlargement is by approximately 6 Å. Because the diffraction peak is almost absent, it is possible that the resulted materials to be exfoliated-intercalated nanocomposites.

All the above-presented results are summarized in Table 3. In 4 cases from 5, the blend diffraction peaks have different intensities than the silicate and the galleries are enlarged with 10–20 Å. The order degree of the resulted materials is smaller or higher because the blends diffraction peaks have different intensities than the silicates alone. With

TABLE 3: The comparison of the XRD diffractograms of the layered silicates with those of the blends PVOH-starch-layered silicates.

PVOH-starch with	No. of the diffraction peaks blend/silicate	Shifted degree of the diffraction angle, ° peak no.1/2/3	Galleries swelling size Å	Diffraction peaks intensity, blend/silicate counts/s/counts/s peak no.1/2/3	Type of the resulted material
Nanocor I 28	2/2	1,83/2,18	20	1. 20/60 2. 40/150	Intercalated/
Nanocor I 33	2/3	1,64/0,85	The same	1.70/70 2.170/120	Intercalated
Cloisite 93 A	2/3	The same	5	110/110	Microcomposites
Cloisite 15 A	2/2	4,8/2,18	9	1.30/0; 2.60/100 3.150/0	Intercalated
Bentonite	1/1	3,80	7,88	50/100	Intercalated
NaMMT	1/2	1,93	18	50/70	Exfoliated-intercalated

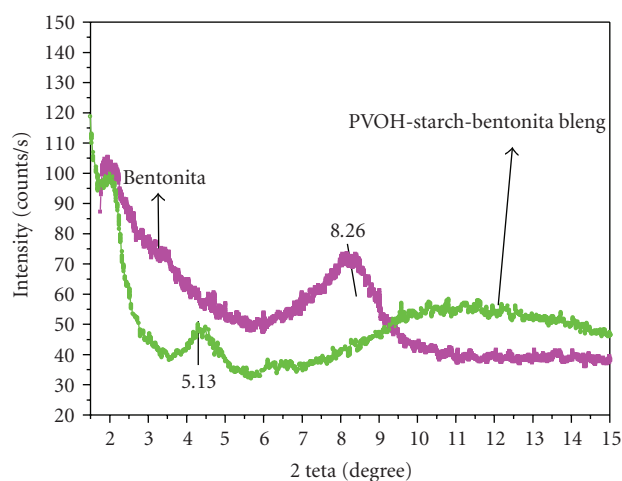


FIGURE 8: The XRD diffractogram of the bentonite and of the PVOH-starch-4% bentonite blends.

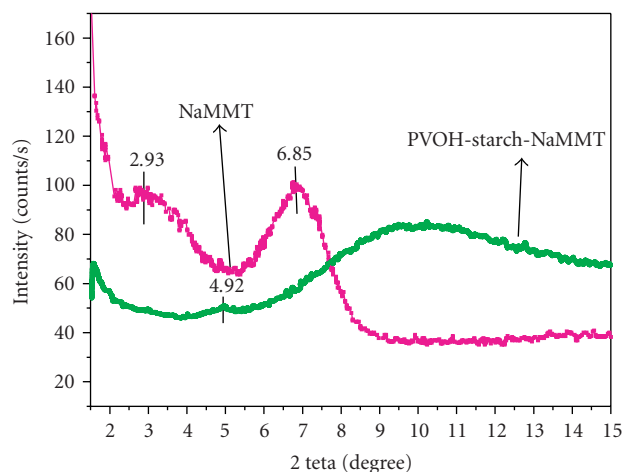


FIGURE 9: The XRD diffractogram of NaMMT and of the PVOH-starch-3% NaMMT blend.

the exception of Cloisite 93 A, in all analyzed situation, the diffraction peaks are shifted toward small angles with $(1, 09-3, 8)^\circ$. Considering the greatest shifting value of the blends diffraction peak, it seems that the better intercalation was registered effects in case of an untreated silicate, NaMMT. If the silicate enlargement size is considered, it seems that better intercalation is produced in case of Nanocor I 28. All these observations seem to lead to the conclusion that in case of the PVOH and starch blends, the degree of intercalation of the two polymers with the layered silicate is increased if layered silicates, untreated or intercalated with ammonium ions that contain small radicals, are used.

Based on the above-mentioned results, neither the silicate exfoliation degree nor the silicate/lamellas dispersion into the polymeric matrix of the new obtained materials can be estimated. The TEM micrographs will bring the necessary information for making estimation about the importance of the silicate galleries treatment, the silicate exfoliation degree, and dispersion within the polymeric matrix and on the nature of the resulted nanocomposites morphology. The TEM micrographs of these blends will be presented in a future paper.

4. CONCLUSIONS

The morphology of the material based on the layered silicate and polymer can be appreciated also based on the XRD diffractograms. The exfoliated nanocomposites are obtained when the XRD diffractograms do not contain anymore the diffraction peaks of the silicates. The intercalated nanocomposites are realized when the diffraction peaks are shifted toward small angles. The microcomposites appear in case of immiscibility of the polymer with the silicate. In this situation, the blend peak is overlapped with that of the silicate.

The XRD diffractogram also gives information about the morphologies of the polymer-silicate materials if the following blend diffractogram characteristics are compared with those of the silicates: number of the diffraction peaks,

shifted degree of the diffraction peaks, diffraction peak intensity, and silicate galleries swollen degree.

In case of the PVOH-starch blends, the degree of intercalation of the two polymers with the layered silicate is increased if the layered silicates is untreated or intercalated with ammonium ions that contain small radicals. If untreated silicate like NaMMT, it is possible to obtain exfoliated nanocomposites. The materials that contain Nanocor I 28 or Nanocor I 33 or Cloisite 15 A are of intercalated nanocomposites type. If the blend of PVOH and starch is reinforced with Cloisite 93 A, microcomposites can be obtained.

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