



SOME ASPECTS CONCERNING THE SILICATE DELAMINATION FOR OBTAINING POLYMERIC BIO-HYBRIDS BASED ON STARCH

Doina DIMONIE,^{a,*} Constantin RADOVICI,^a Inna TRANDAFIR,^a Simona Florentina POP,^a Irina DUMITRIU,^a Radu FIERASCU,^a Luiza JECU,^a Celina PETREA,^b Catalin ZAHARIA^b and Ramona COŞEREÀ^a

^a ICECHIM Bucharest, 202 Splaiul Independentei, Bucharest 060021, Romania

^b “P.Poni” Institute, 41 Aleea Grigore Ghica, Iași 700487, Romania

Received August 6, 2009

The structure and properties of the bio-hybrids based on starch and PVOH obtained with MMT conditioned before melt processing into a good plasticizer depends on the conditioning sequence characteristics. A small influence on the silicate morphology can be a sign that the silicate was only hydrated by water and it is not yet dispersed into water. The stirring of multilayered silicate into a good starch and polyvinyl alcohol plasticizer in a special mechanical sequence is a good method to increase the silicate exfoliation.

INTRODUCTION

Bio-nano-composites are an emerging group of nano-structured hybrid materials that outcome by combination of natural and synthetic polymers with inorganic solids. Bio-nano-composites show, at least, one dimension at nanometric scale.¹⁻⁶ The bio-hybrids exhibit improved structural and functional properties of great interest for many and distinctive applications.⁷⁻¹⁰

The usage of the starch for polymeric packages manufacture replies to a sharp demand of the contemporary society for regenerative and/or alternative resources. Because of the water solubility of the PVOH and of the starch biodegradability, green packages based on these two polymers can be obtained.¹¹

The performing of the bio-hybrids considering starch, polyvinyl alcohol (PVOH), and multilayered silicates through melt processing techniques is not an easy task. The obtaining, in this way, of these bio-hybrids is conditioned by many parameters. For instance, it was observed that the homogeneity of the blends, besides the

characteristics of the melt processing equipment, depends on blending ratio, nature of the individual component treatments, melt processing sequence and conditions, nature of the used melt processing additives.¹¹⁻¹⁵

The degree of intercalation of these bio-hybrids is increased if treatment with ammonium ions silicate as Nanocor I 28 is used.¹¹⁻¹⁵ If untreated silicate like Na Montmorillonite (NaMMT) is utilized it is possible to obtain exfoliated – intercalated nanocomposites.¹⁴ These bio-hybrids may have a non-homogenous thermal behavior, if the silicate was no treated.¹² In this case the melt takes place in extremely wide temperature range from 143 °C to 235 °C, in a broad melting endotherm that contains many shoulders.¹¹⁻¹⁵

The starch melt processing needs, firstly, to destroy the polymer crystallinity, a process known as pre-jellifying, destructuring, melting etc.¹² The effect of clay – water interactions on swelling in montmorillonite clay was studied in.¹⁶⁻²⁵ In²³ it was found that the uptake of water by sodium montmorillonite appears to be controlled by the competitive hydrogen bonding between water molecules and silica tetrahedral. As a consequence

* Corresponding author: ddimonie@rdslink.ro; ddimonie@icf.ro

of the hydration, diffusion and osmosis multilayered silicate delamination can take place (Fig. 1).

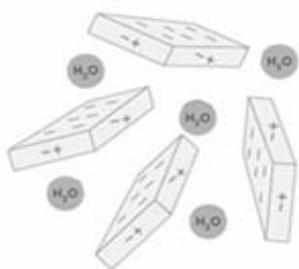


Fig. 1 – The possibility of MMT delamination based on the interaction with water.

The water can be a good plasticizer for the PVOH – starch polymeric system.^{13,26-28} Considering the plasticizing formula and the conditioning of multilayered silicate into water in a sequence that antecedes the obtaining of bio-hybrids based on starch, PVOH, and multilayered silicate (MMT), the possibilities to increase the multilayered silicate exfoliation and the resulted lamellae dispersability into the polymeric matrix were studied.

The influence of the characteristics of the conditioning sequence of multilayered silicate into water on the multilayered silicate exfoliation is presented. The conditioning sequence antecedes the obtaining of the bio-hybrids based on starch through melt processing procedure.

EXPERIMENTAL

Bio-hybrids based on starch, polyvinyl alcohol (PVOH), and multilayered silicates were obtained by melt compounding the two polymers with reinforcing agent and proper processing additives.

The following materials were used: Polyvinyl alcohol with hydrolyze degree of 99 moles %, 0.5 – 1.8 % residual polyvinyl acetate, 27 – 33 cP viscosity, 1674 J / kg·K specific heat, vitreous transition at 82 °C, melt temperature of 255 °C, and crystalline content by 30.6%; Native starch from maize with 13.1% humidity, 2.2 % acidity, 4.9 pH, 70 °C vitreous transition, 263 °C melt temperature, 32% crystalline content; Multilayered silicate treated with trimethyldodecadecylammonium silicate (Nanocor I 28) and untreated silicate (NaMMT); ordinary melt processing additives.

The conditioning of the multilayered silicate was done, in water, before melt processing, without mechanical stirring in procedure A and with mechanical stirring in procedure B. In both situations it were used the same compounding formula and the same plasticizers quantity.

In procedure A the following three bio-hybrids (a, b, c) were obtained: Bio-hybrids a – do not contain water and were plasticized with glycerol; Bio-hybrids b – were plasticized with a blend of 50 % glycerol and 50 % water. Before melt processing,

all the blend components were manually mixed in solid state; Bio-hybrids c – were plasticized with a blend of 50 % glycerol and 50 % water. The bio-hybrids components were not manually mixed in solid state.

In procedure B the multilayered silicate was conditioned with water, under stirring 8h, 16 h, 24 h, 76 h, 288 h and then was incorporated, by melt processing techniques, into the polymeric matrix using the same formulation and the same plasticizers quantity as in A procedure.

The characterization of the compounds was made by DSC and XRD. The recordings of the DSC thermograms were carried out on a Du Pont 990 DSC analyzer by heating from 30 to 220 °C with 10 °C/min. The XRD diffractograms were recorded on a DRON 2, 0 X-ray diffractometer at room temperature. The variation of the radial diffraction intensity dependence on the diffraction angle (2 theta) was recorded. The working conditions were: step size by 0.03° (2 theta), scanning rate = 8s/step, filter with $\lambda=1.7921 \text{ \AA}$, and diffraction range 2-15° (2 theta). The interbasal spacing was calculated based on the Bragg Law ($n\lambda=2ds\sin\theta$, 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).

RESULTS

The obtained results depends on the nature of the silicate treatment.

In A procedure there are not significant differences between the three obtained bio-hybrids that have almost the same morphologies (Fig. 2) and because of this, approximately the same thermal behavior (Fig. 3). The chemically treated multilayered silicate Nanocor I 28 that was used for obtaining the three bio-hybrids according to procedure A has three diffraction maximums at 1.76; 4.2; 6.36° and a highest intensity by 60 count/s.

In case of the bio-hybrids with 4 – 5 % silicate the diffractions from 1.76° and 6.36° of Nanocor I 28 disappear and remain 2 diffraction peaks within the interval 2° – 4.4°, by 100 counts intensity for the bio-hybrids that contain water and by 80 counts/s for those that were plasticized only with glycerol.

The movement of the diffraction peaks of the bio-hybrids towards small angle reveals certain interactions between the silicate and the two polymers that means that the obtained materials have own morphologies, other than those of individual polymers.

The morphology of the new compounds obtained according to A procedure determines the differences between the thermal behavior of the two polymers and the three bio-hybrids. The melt temperature of PVOH and starch is 258 °C and 263 °C (Fig. 3a). This temperature decreases till 210 – 215 °C in case of the bio-hybrids with 3 % and 5 % treated silicate (Fig. 2b).

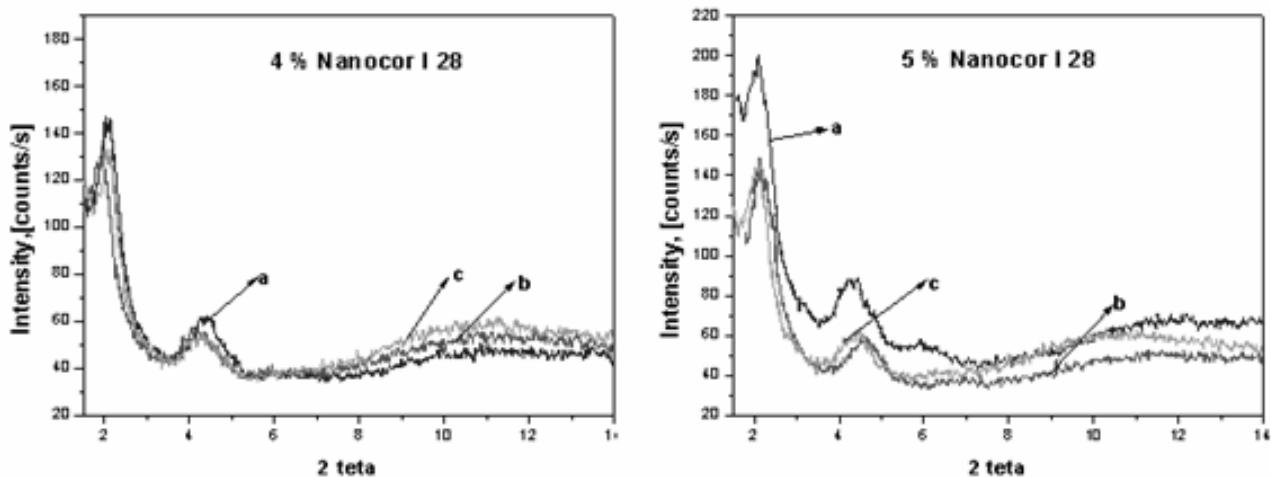


Fig. 2 – The XRD diffractograms of the three bio-hybrids obtained in A procedure.

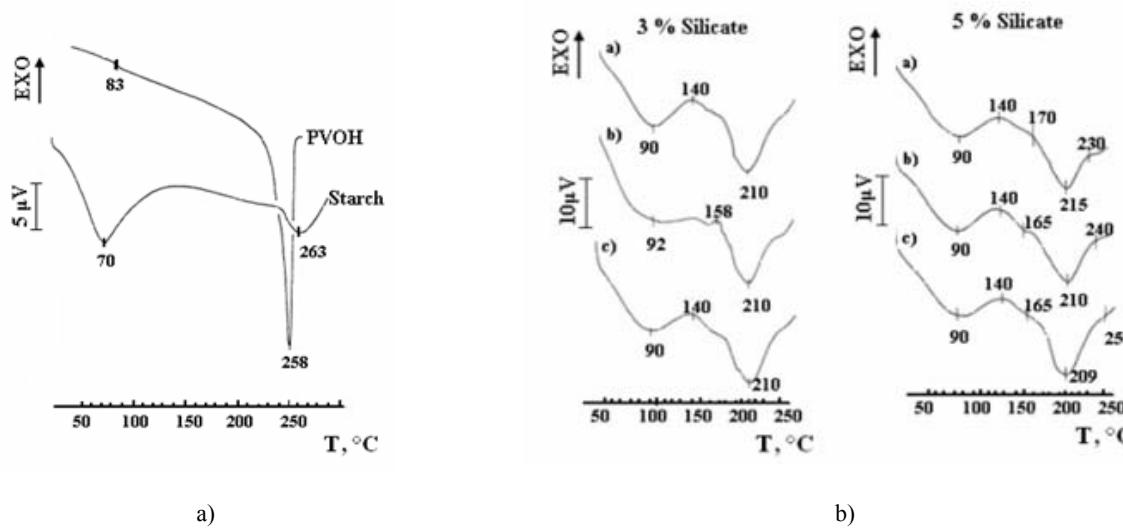


Fig. 3 – The DSC curves of PVOH, starch (a) and the three bio-hybrids obtained in A procedure (b).

If the blend of PVOH with starch and multilayered silicate is not plasticized with water, then the melting is done in a narrower interval with a deep melting endotherm. If the mixture is plasticized with water and the silicate was pre-dispersed in advance into water, the melting is produced at higher temperatures, in a wide interval, less deep. This may demonstrate that at the same composition, the usage of the water as plasticizer and the MMT pre-dispersion in advance seems to contribute to a better bio-hybrids homogeneity. The dispersion of MMT in water looks to improve the bio-hybrids homogeneity

Figs. 2 and 3 demonstrate that the multilayered silicate exfoliation according to A procedure is still

not enough. The diffractions peaks of the three bio-hybrids is nevertheless too high and tight.

In²⁹ it was demonstrated that the differences between the FTIR spectra of the bio-hybrids that contain treated and untreated silicate are very small (Fig. 4). These spectra prove that the differences between the two situations are not significant. For this reason NaMMT multilayered silicate was used for obtaining bio-hybrids according to B procedure.

The diffractogrammes of the bio-hybrids obtained according to B procedure are entirely changed as those of the bio-hybrids resulted considering A procedure (Fig. 5 and Table 1).

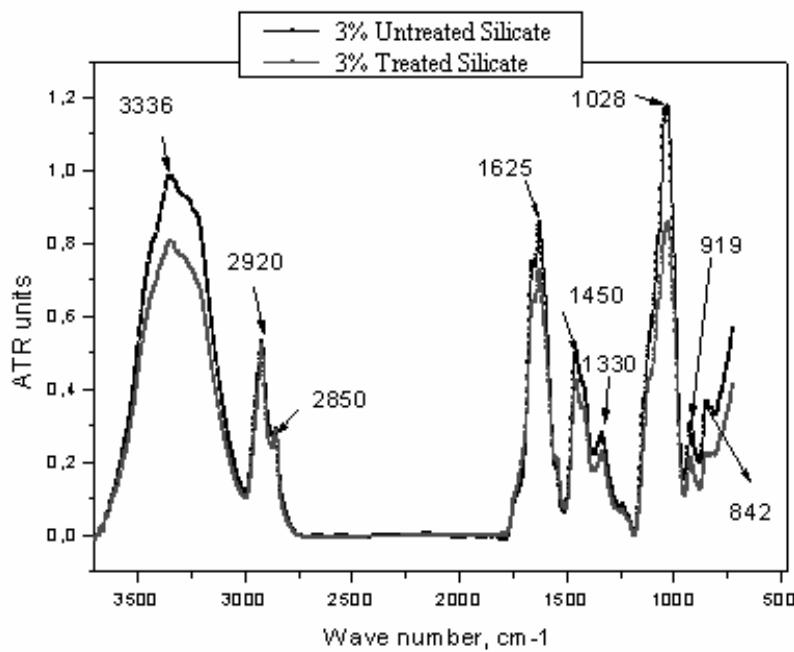


Fig. 4 – The FTIR spectra of the bio-hybrids with untreated and treated silicate.

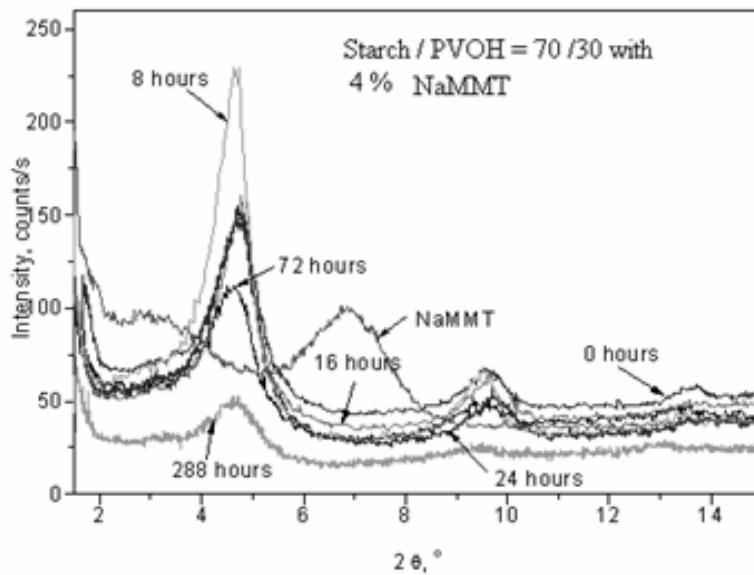


Fig. 5 – The XRD diffractograms of the bio-hybrids obtained according to B procedure.

Table 1

The characteristics of the diffractograms of the bio-hybrids obtained according B procedure

Pre-treatment, h	2θ °	Peak intensity, counts/s	d, Å
NaMMT			
0	3.01 / 6.93 4.70 / - / 9.44	98.14 / 100.47 154.95 / - / 67.78	12.77 / 29.35 18.8 / - / 9.37
8	4.72 / - / 9.47	229.27 / - / 67.34	18.7 / - / 9.34
16	4.77 / - / 9.58	160.18 / - / 65.45	18.52 / - / 9.23
24	4.68 / - / 9.37	147.83 / - / 54.99	18.9 / - / 9.44
72	4.65 / - / 9.32	110.93 / - / 51.72	19 / - / 9.49
288	4.63 / - / 9.57	53.64 / - / 28.10	19.08 / - / 9.24

The shape of the diffractograms of the new bio-hybrids is different from that of NaMMT. The bio-hybrids diffraction peaks are shifted towards small angles (3.01° and 6.93° in the case of silicate and $\sim 4.6^\circ$ and $\sim 9.57^\circ$ for bio-hybrids) and have smaller intensities much more the silicate conditioning time is longer. The NaMMT peak of 3.01° does not appear. The new materials have a new diffraction peak at around 9.44° by 154. 95 counts/s. If the NaMMT peak of 6.93° diffraction has an intensity of 98.14 counts/s, the peak of the new materials is shifted to around 4.7° and has a diminished intensity by 28. 10 counts/s if NaMMT was treated 288 hours. The intensity of this peak can decrease down to 53. 64 counts/s if the silicate has been treated for 288 hours; that means a decrease in the intensity of this peak by almost 65% due to the used conditioning procedure.

The montmorillonite delamination and the uniform dispersion of the resulted lamellaes into the polymeric matrix is the main requirement that ensures the obtaining of byo-hibrids by nanocomposite type. Taking into consideration these two aspects it can be estimated that after A procedure the silicate is not entirely exfoliated. It is possible that the small influence upon the structure and properties of the new bio-hybrids that contain MMT pre-dispersed into water can show that the MMT was only hydrated by water and it was not dispersed into water.

According to the XRD measurement, because the diffraction peak has still a very small intensity, it seems that in procedure B the silicate is almost, but not entirely, exfoliated. It is possible that a longer treatment according to procedure B or a new procedure in more accelerated delamination conditions should determine the silicate delamination.

It may be possible that the finding of better delamination conditions of the MMT into water in a procedure that anteceds the bio-hybrids obtaing step, can ensure the obtaining of bio-hybrids by exfoliated nanocomposite type, based on starch and multilayered silicate.

However, the stirring of multilayered silicate into a good starch and polyvinyl alcohol plasticizer in a special mechanical sequence can be a good method to increase the silicate exfoliation.

These results impose new experiments for a better control of the MMT dispersion into water. These new experiments can be more eloquent in realizing bio-hybrids with nanostructurated morphologies based on starch.

CONCLUSIONS

The influence upon the structure and properties of the bio-hybrids obtained with MMT dispersed into water before melt processing depends on the conditioning sequence characteristics. A small influence on the morphology can be a sign that the silicate was only hydrated by water and it is not yet dispersed into water. The stirring of multilayered silicate into a good starch and polyvinyl alcohol plasticizer in a special mechanical sequence is a good method to increase the silicate exfoliation. These results impose new experiments for a better control of MMT dispersion into the selected starch and PVOH plasticizer. These new experiments can be more eloquent in obtaining bio-hybrids based on starch with nanostructurated morphology.

REFERENCES

1. S. Thomas and G. E. Zaikov, "Progress in Polymer Nanocomposite", Nova Science Publishers Inc, 2008.
2. L. A. Utracki, "Clay-containing polymeric nanocomposites", Rapra Publishing House, 2004.
3. Y-W. Mai and Z-Z. Yu, "Polymer nanocomposites", Woohead Publishing Limited, 2006.
4. A. Leszczynska, J. Njuguna, K. Pielichowski and J.R. Banerjee, *Therm. Acta*, **2007**, 453, 75-96.
5. A. Leszczynska, J. Njuguna, K. Pielichowski and J.R. Banerjee, *Therm. Acta*, **2007**, 454, 1-22.
6. Z.M.O. Rzaev, A. Yilmazbayhan and E. Alper, *Adv. Polym. Tech.*, **2007**, 26, 41-55.
7. J. Koo, "Polymer Nanocomposites: Processing, Characterization and Applications", Printed by Donnelly, 2006.
8. M. Darder, *Adv. Mater.*, **2007**, 19, 1309-1319.
9. M. Dimonie, *Rev. Roum. Chim.*, **2005**, 527-534.
10. M. Knite, V. Teteris, B. Polyakov and D. Erts, *Mater. Sci. Eng. C*, **2002**, 19, 15-19.
11. D. Dimonie, C. Radovici, S. Serban, A. Tararu and G. Vasilievici, *Mater. Plast.*, **2007**, 44, 148-154.
12. D. Dimonie, C. Radovici, C. Zaharia, G. Vasilievici and A. Stoleriu, *Mater. Plast.*, **2006**, 43, 132-137.
13. D. Dimonie, D. Petre, Vasilievici Gabriel (ICECHIM Bucuresti), Patent RO 121692, 2008.
14. D. Dimonie, C. Radovici, G. Vasilievici, M.C. Popescu and S. Garea, *J. Nanomater.*, **2008**, doi:10.1155/2008/538421.
15. D. Dimonie, I. Kelnar, C. Duncianu, R.M. Coserea, F.S. Pop, I. Dumitriu, M.C. Popescu and C. Zaharia, *Proceeding of 16th Roumanian International Conference on Chemistry and Chemical Engineering*, Sinaia, September 9-12, **2009**.
16. P. Colonna, "A Chimie Verte", Edition TEC & DOC, Lavoisier, 2006.
17. X. Tang, S. Alavi and T.J., Herald, *Carbohyd. Polym.*, **2008**, 74, 552-558.
18. W. Ning, Z. Xingxiang, H. Na and B. Shihe, *Carbohyd. Polym.*, **2009**, 76, 68-73.
19. http://en.wikipedia.org/wiki/Clay-water_interaction
20. <http://www.glossary.oilfield.slb.com/Display.cfm?Term=clay-water%20interaction>

21. http://www.absoluteastronomy.com/topics/Clay-water_interaction
22. A.C.D. Newman, "The interaction of water with clay mineral surfaces", in: A.C.D. Newman (Ed), "Chemistry of Clays and Clay Minerals, Mineralogical Society Monograph 6", 1987, p. 237-274.
23. <http://www.ce.washington.edu/em03/proceedings/papers/812.pdf>.
24. C.L. AMORIM, *Nucl. Instrum. Methods.*, **2007**, 580, 768-770.
25. http://www.engr.usask.ca/classes/CE/468/notes/468-2_ClayMin.pdf.
26. C.A. Finch, "Polyvinyl Alcohol – Properties and Applications", Wiley and Sons, London, 1983, Chapter 8, p. 167-183; Chapter 9, p. 203-233.
27. L. Mao, S. Imam, S. Gordon, P. Cinelli and E. Chiellini, *J. Polym. Environ.*, **2000**, 8, 205-211.
28. M.A.L. Russo, R. Truss and P.J. Halley, *Carbohyd. Polym.*, **2009**, 77, 442-448.
29. D. Dimonie, I. Kelnar, R. Socoteanu, R. N. Darie, F. S. Pop, C. Zaharia, C. Petre, M. Nemteanu and R. Coserea, *Mat.Pl.*, **2010**, 486-491.