

THE POLYMER MOLECULAR WEIGHT AND SILICATE TREATMENT INFLUENCE UPON THE MORPHOLOGY OF NANOCOMPOSITES FOR FOOD PACKAGING

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Some results concerning the obtaining, based on melt processing techniques, of polymer nanocomposites from poly(ethylene-co-vinyl acetate) and layered silicates with improved barrier properties for food packaging it is presented. The dependence between the polymer molecular weight and the silicate treatment upon the EVA – layered silicates micro-composites morphology is analyzed.

As a consequence of the unmetability in proportion with the molecular weight, microcomposites with high morphological level order are obtained if EVA with high molecular weight was used.

Because of the prevalent hydrofobicy of the EVA chains with 28 % polar groups, the biggest silicate “swelling” are obtained with untreated silicates. If the silicate was functionalised, then, from ammonium and pirolydonym ions, the ammonium with small substituents must be preferred. In the case of big substituents the interactions with the vinyl-acetate group from EVA are weak and the silicate “swelling” degree unimportant.

INTRODUCTION

If, between the 1950 and 1995, it was the period of “macro” materials in which the leading size was the millimeter, around the 1970s, started the stage of micro-materials that have as characteristic feature the micro-meter. In 2005, begin the “nano” time that, is estimated to have an extremely long life, at least until after 2050. The main characteristics of the “macro” period were the interest for the miniature sizes. The stars of “nano” period are and will be the nano-materials, nanocomposites and biotechnologies. The main applications of “nano” materials are the packaging, the automotive industry and the constructions and in the next years, medicine, micro-electronics and still packaging.¹⁻³

Many packed foods, needs, on the one hand, protection against oxygen, humidity, light, and on the other hand, the preservation of their aromes

and fats, on the entire life, *i.e.* until food-stuffs consumption. The needed food-stuffs protection, is provided by the packaging barrier properties defined by the performance level, presented in table 1.

The most known packaging with the barrier properties are made of polymeric nanocomposites, and montmorillonite (MMT), a layered silicate with the thickness at the nano scale and with the width and length within the micrometers range.

Whereas, the nanocomposite permeability is expressed by the formula (1) and the passing of gases through the nanocomposite, follows the “sinous path of Neilson” (fig. 1), the **nanocomposites used as** materials with the barrier properties must be of the **exfoliated type** (fig. 2).

$$P_{\text{nano}} = (1 - \varphi) P_{\text{matrice}} / (1 + \alpha \varphi / 2)^* \quad (\text{formula 1})$$

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where: P_{matrix} = polymer permeability; P_{nano} = nanocomposite permeability; ϕ = fraction of

volume for the nanoparticles; α = ratio related to the particles shape

Table 1

General estimation of the performance levels of the barrier properties for the food packaging

Performance of barrier	Light optic Density	OTR ^a , cm ³ /m ² d bar	WVTR ^b , G/m ² d
High	> 2.8	< 1.0	< 0.5
Medium	2.0 – 2.8	1.0 – 10	0.5 – 5
Low	< 2.0	> 10	> 5

^a OTR – oxygen transmission rate; ^b WVT – water vapor transmission

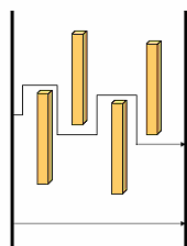


Fig. 1 – The illustration of sinous path of Neilson.

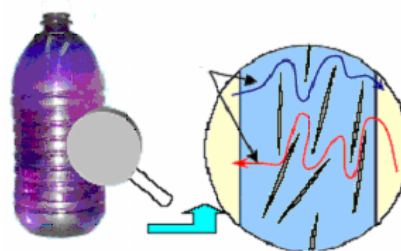


Fig. 2 – The explanation of the necessity to perform exfoliated nanocomposites for maximizing the barrier properties.

The maximizing the barrier properties of a polymer nanocomposite, achieved by the melt processing techniques, require the solving of the following scientific and technical aspects: the compatibilisation of the silicate with the polymer matrix based on the silicate treatment, the melt compounding, inclusively by reactive techniques, of the treated layered silicates with the interest polymeric matrix; the exfoliation of the layered silicate until individual lamellas, the barrier effect maximizing by the orientation, at the melt processing, of the lamellas within the polymeric matrix, parallel with the package surface, the avoiding of the lamellas re-aggregation during the packaging manufacture (films or bottles). The

packaging obtaining must avoid loosing of silicates exfoliation and lamellas orientation. Also it must be done the characterization of the nanocomposites and packaging by using the advanced nano-scale evaluation methods and devices and the estimation of the physico-mechanical properties, thermal stability and barrier properties with visualisation of the morphologic structures in relation to the obtained properties.

The polymer nanocomposites with improved barrier properties, are used both, as films and as adhesives. The multi-layers structures (fig. 3) with improved barrier properties are extensively used in the packaging production.

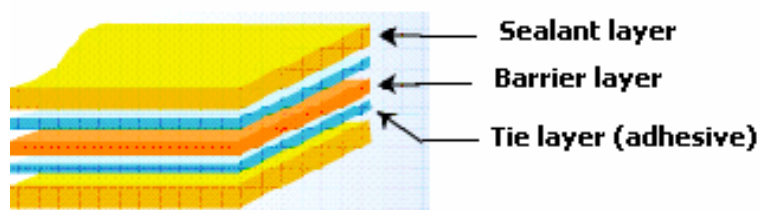


Fig. 3 – Multilayer polymeric structure used as food packaging.

The ethylene–vinyl acetate co-polymer (EVA) can be used as a layer with barrier properties and as an adhesive intermediary layer within the composition of the multi-layered structure designed for the packaging production.⁴⁻⁸

A part of the results obtained for the preparation, by the melt processing techniques, of multi-layers food packaging with the improved barrier properties, from nanocomposites based on the ethylene – vinyl acetate copolymer (EVA) and montmorillonite (MMT), will be presented below.

EXPERIMENTAL

The aim of the performed works was the study of the EVA molecular weight and of the silicates treatment influence upon the EVA – MMT composites morphology. As it is known, depending on the silicate exfoliation degree, the resulted polymer–silicates systems can be of the following types: micro-composites or the conventional composites (fig. 4a),

intercalated nanocomposites (fig. 4b) and exfoliated nanocomposites (fig. 4c).⁹ Because the results shown below, do not refer to the TEM micrography, on which basis, good estimations upon the morphology type can be made, for discussing the obtained polymer – silicate systems the micro-composite nomenclature will be used in the following presentation.

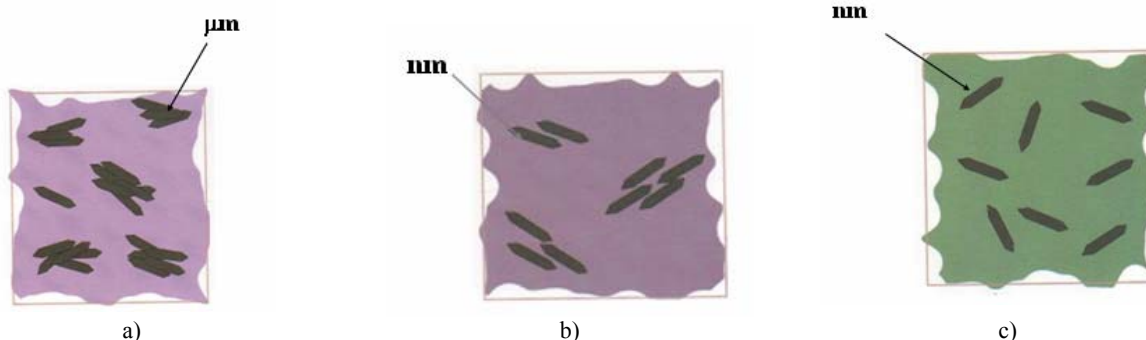


Fig. 4 – Types of layered polymer–silicate systems: a) microcomposites (polymer are not intercalated between the silicate layers); b) intercalated nanocomposites (polymer chains are intercalated between the clay layers); c) exfoliated nanocomposites (the clay layers are completely distributed in the polymer matrix).^{8,9}

1. Materials

a. The ethylene–vinyl acetate copolymer with different molecular weights, provided by the Du Pont company (Table 2). Knowing that the most technological expression of the molecular weight is the melt flow index (MFI),¹⁰ the reference at different EVA molecular weight, will be done using the MFI values.

b. Treated and non- treated montmorillonite (Tables 3, 4 and fig. 6). The used silicates have not a homogeneous morphologies, because they contain galleries with different sizes, except of bentonite and Cloisite 15 A.

c. Additives for the EVA melt processing.

Table 2

The used EVA types

Grades / Applications	Vinyl acetate content, [%]	Tmelting, °C (Boetius)	MFI, g/10 min.	Density, g/10 min.	Hardness, °Sh A
Elvax 260 / industrial application	28	78 – 85	6	0.955	85
Elvax 220 W/ industrial application	28	65 – 70	150	0.951	69
Elvax 210 W / industrial application	28	62 – 65	400	0.951	62
Elvax 205 W / industrial application	28	60 – 70	800	0.951	75

Table 3

Treated and non- treated montmorillonite

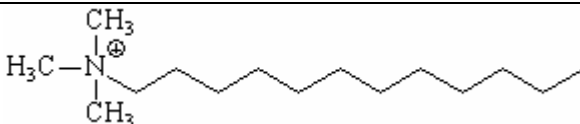
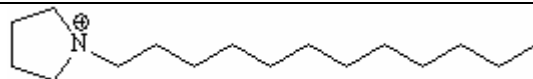
Silicate grades	Chemical formula	XRD basal spacing, Å
Bentonite	natural, non-functionalised Montmorillonite $M_x Al_{4-x} Mg_x Si_8 O_{20} (OH)_4$ (M= monovalent cation; x = degree of isomorphous substitution (values 0.5 – 1.3))	11.7
Nanocor I 28 ¹¹	 Trimethyl dodecyl ammonium Particles with the diameter of 8–10 μm with density of 1,9 g/cm ³ ¹⁰	28
Nanocor I 33 ¹¹	 Dodecyl pyrrolidone	30.29

Table 3 (continued)

Cloisite 15 A	Dymethyl, 2-ethylhexyl (hydrogenated tallowalkyl) ammonium Hydrogenated tallow: ~ 65 % C 18; ~ 30 % C16; ~ 5 % C14 $\begin{array}{c} \text{HT} \\ \\ \text{H}_3\text{C}-\text{N}^{\oplus}-\text{CH}_3 \\ \\ \text{HT} \end{array}$ HT = Hydrogenated tallow	31.5
Cloisite 93 A	$\text{CH}_3\text{N}^+(\text{HT})_2\text{H}$ Hydrogenated tallow: 65 % C; ~ 30 % C 16; ~ 5 % C14 Anion: HSO_4^- $\begin{array}{c} \text{HT} \\ \\ \text{H}_3\text{C}-\text{N}^{\oplus}-\text{HT} \\ \\ \text{HT} \end{array}$ Methyl dihydrogenated tallow ternary ammonium	23.6

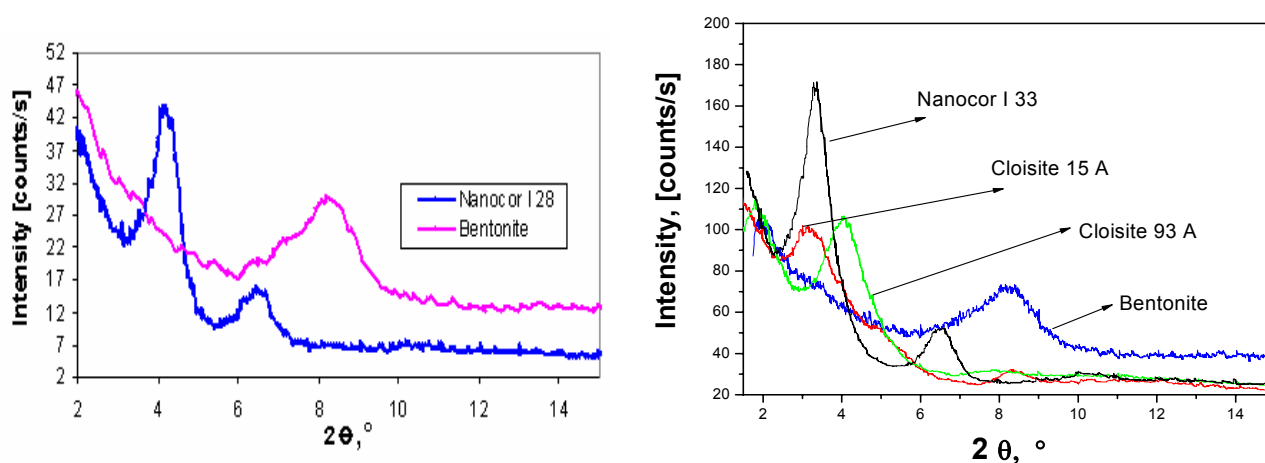


Fig. 5 – The diffractograms of the used silicates.

Table 4

The XRD basal spacing

Silicate	2 teta, °	d, Å
Cloisite 15 A	3.21; 8.24	31.9
Cloisite 93 A	1.78; 4.05; 7.9	57.6; 25.3 ; 13
Nanocor I 28	1.76; 4.2; 6.36;	58; 24.4 ; 16.1
Nanocor I 33	3.35; 6.64; 10.8	30.6; 30.29 ; 30.23
Bentonite	8.26;	12.43

2. Microcomposites obtaining

Compounding within a Bradender plastographs at 125 – 130°C, 100 rpm and outlining in sheets, by rolling on without friction on a laboratory roller has been employed.

3. Characterisation

The morphology was analysed by X rays diffraction (RDX). It was recorded the variation of the radial diffraction intensity dependence by the diffraction angle, at the room's temperature. It was explored the 2 – 14 ° diffraction angle domain, working with 0.03° step, scanning speed = 8 s /step, and a filter with $\lambda = 1.7921 \text{ \AA}$. For computing the interbasal distance (d) it was used the Law of Bragg¹² (formula 2).

$$d = n\lambda / 2 \sin \theta \quad (\text{formula 2})$$

where: d – basal spacing; n – constant; λ – wavelength of X ray; θ – the angle between the incident ray and the diffusion plane.

RESULTS

The X rays diffractograms of the micro-composite obtained from EVA with different molecular weight and Cloisite 15 A are presented in fig. 7. The XRD basal spacings on these microcomposites are presented in table 7.

The diffractograms show, for all the situations, an identical arrangement of the amorphous morphology, at **10.06 Å**.

It is also noticed that, regardless the value of the polymer molecular weight, the diffraction takes place, in all cases, approximately at the same diffraction angles (5.13 Å and 2.53 – 2.66 Å). Depending on the EVA molecular weight, the diffractograms differ each other, by the height, width and the area of the diffraction peaks. The smallest diffraction peaks, are met for the microcomposites in which EVA has the smallest

molecular weight (MFI= 800 g/10 min.). The height of the 2.53 Å diffraction peak is approximately 50 counts/s, that means approx. 3 times lower than the similar peak from 2.66 Å of the micro-composite in which the polymer has the biggest molecular weight (MFI = 6 g/10 min.). These results show a dependence with the polymer molecular weight of the order degree of the morphological structures that have the same diffraction maximum. So much less the area of the diffraction peak, more reduced the order degree of the sample morphology.

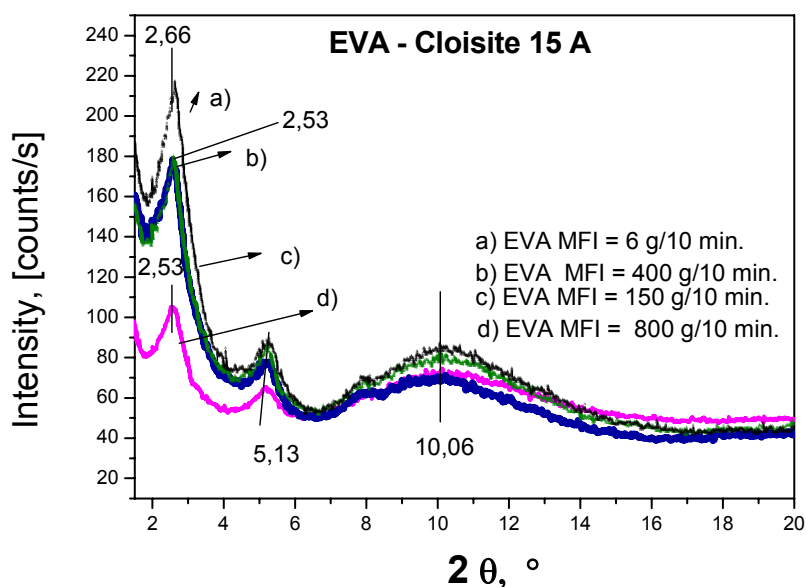


Fig. 6 – The XRD diffractograms related to the microcomposites of EVA with different molecular weights and 3 % Cloisite 15 A.

Table 5

The XRD basal spacing of the micro-composites of EVA with different molecular weights and 3 % Cloisite 15 A

EVA MFI, g/10 min.	2 teta, °	Dx, Å
6	2.56; 5.14; 7.71;	40.1; 20; 13.3
150	2.58; 5.18;	39.7; 19.8
400	2.62; 5.24;	39.1; 19.6
800	2.62; 8.21	39.1; 19.6

^x Bolded Value = main gallery

According to fig. 5 and Table 4, Cloisite 15 A is a silicate with a homogeneous morphology, because it has only one basal spacing size, respectively of **31.9 Å**. Within the EVA micro-composites, Cloisite 15 A suffered a spacing until **40.1 Å** in case of EVA with MFI = 6 g/10 min. and until **39.1 – 39.7 Å** for EVA with lower molecular weights (table 5). All the performed microcomposites are inhomogeneous because they contain galleries with different sizes.

Comparing the basal spacing size of the Cloisite 15 A in the native condition, to those from the micro-composites with EVA with different molecular weights, it is noticed that through the melt compounding, it was achieved an increase of the basal spacing size of **7 – 8 Å**. This means that the interactions between the acetate group from the copolymer with the ammonium groups from the Cloisite 15 A galleries, determined galleries spacing of approx. **8 Å**.

The X rays diffractograms of the micro-composites based on EVA with different molecular weights and 4 % Cloisite 93 A are presented in the fig.7. The basal spacings of these micro-composites are shown in Table 5.

An identical ordness of the amorphous phase, at approx. 10 Å distance, in all situations can be observed. Regardless of the polymer molecular weights, the diffraction take place at the same angles (approx. 5.62 Å and approx. 2.96 Å respectively). The height, width and diffraction

peak area make the differences between the diffractograms (fig.7). The smallest diffraction peaks are recorded for the micro - composite in which the polymer has the smallest molecular weight (MFI= 800 g/10 min.). It can be observed, in this situation too, the dependence of the order degree of the morphological structures which the same diffraction peaks on the molecular weight. Much the diffraction peak has a smaller height, more the order degree is lower.

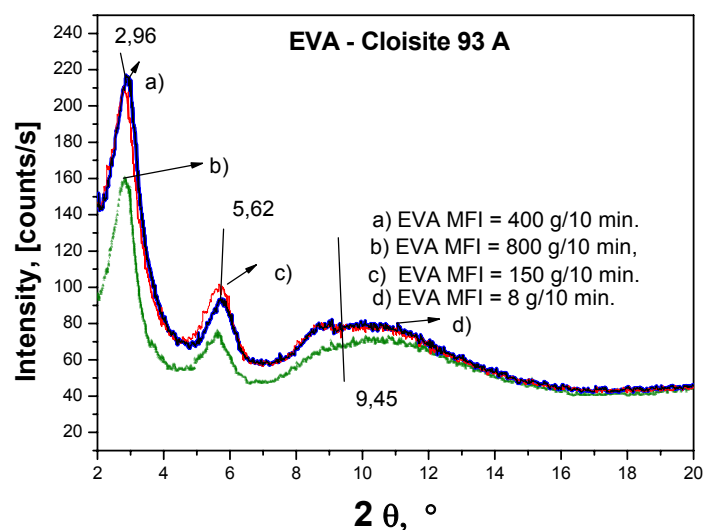


Fig. 7 – The X rays diffractograms for the EVA micro - composites with different molecular weight and 3 % Cloisite 93 A.

Table 6

The XRD basal spacing of the micro- composites of EVA with different molecular weight with 3 % Cloisite 93 A

EVA MFI, g/10 min.	2 teta, °	D ^x , Å
6	2.93; 5.79	35 ; 17.7;
150	2.85; 5.68;	36 ; 18.1;
400	2.88; 5.74;	35.6 ; 17.9;
800	2.88; 5.74;	35.5 ; 17.9;

^x Bolded Value = main gallery

Cloisite 93 A is a silicate with a non-homogeneous morphological structure as it contains galleries of different size (basal spacing by 57.6; **25.3**; 13 Å) (fig. 5, table 4). The morphological order of the 4 micro - composites with EVA does not depend on the molecular weights (fig. 7, table 6). All these micro-composites have a similar morphological order with galleries of about **35 – 36 Å** and **17 – 18 Å**. This means that the gallery spacing, in all cases, is by approximately **10 – 11 Å** regardless the EVA molecular weight.

Considering the Cloisite 15 A and Cloisite 93 A degree of “swelling“ into the studied micro - composites, it can be underlined that the interactions between the vinyl acetate groups from EVA and the functional groups from the Cloisite 15 A and Cloisite 93 A galleries are characterized by small values and order of magnitude.

The X rays diffractograms of the EVA - Nanocor I 28 micro - composites, are presented in the fig. 8 and their basal spacings in the table 7. These diffractograms show, for all the variants, an identical order of the amorphous phase, at a distance of 10.1 Å. The micro - composite

diffractogram in which the polymer has the biggest molecular weight (MFI = 6 g/10 min.) does not show any maximum of diffractions (fig. 8, a curve). If the polymer has a smaller molecular weights (MFI = 150, 400, 800 g/10 min.) then the diffractograms put into evidence the diffractions at the same angles for all the three different situations (2.21 - 2.39 Å and at 5.04 Å). These values are different from those of the individual silicate and shifted to small values of the diffraction angle.

These peaks have a small height (50 – 90 counts/s) and a similar width. The different height of the diffraction peaks from 2,21 - 2,39 Å indicates greater morphological order in case of the polymer with a higher molecular weights. Practically, the height of these peaks decrease with the decreasing of the polymer molecular weight. The diffraction peak of the micro-composite in which the polymer has the lower molecular weight (MFI = 800 g/10 min.) is by the smallest height.

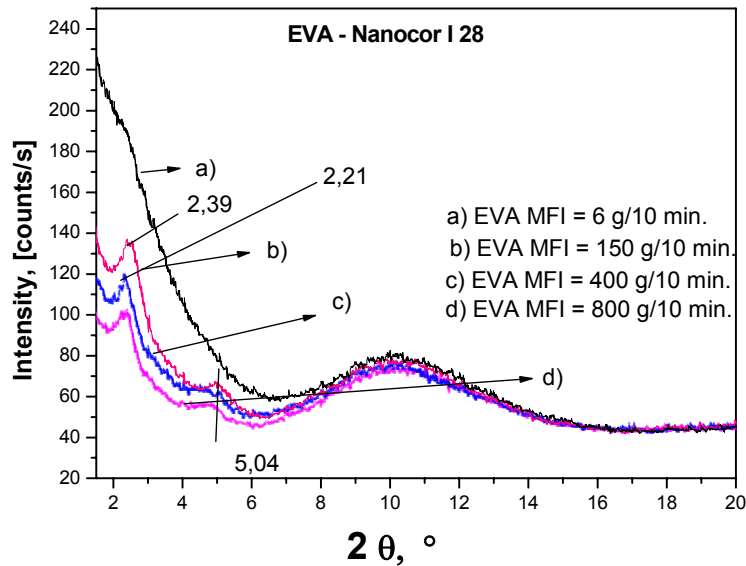


Fig. 8 – Diffractograms of X rays for the EVA microcomposites with different molecular weight and 3 % Nanocor I 28.

Table 7

The XRD basal spacing of the micro-composites of EVA with different molecular weights and 3 % Nanocor I 28

EVA MFI, g/10 min.	2 teta, °	d, Å
6	-	-
150	2.38; 4.8;	43.5; 21.5
400	2.32; 4.65;	44.2; 22.1
800	2.48; 4.95;	41.4; 20.7

Comparing the basal spacing of Nanocor I 28 in the native state with those from the EVA micro-composites, it can be noticed that by melt processing with EVA, a silicate “swelling” by 16 – 20 Å (the basal spacings of 24.4 Å in native state and of 41 – 44 Å in micro-composites) was performed. This means that the functional groups from the Nanocor I 28 galleries, interact more efficiently with the acetate groups from EVA than in case of the other silicates (Cloisite 15 A and Cloisite 93 A). In other words the substituents from the ammonium ion used for the layered

silicate galleries treatment, control the interaction with the polymer.

The X rays diffractograms of the EVA micro-composites with the **Nanocor I 33**, are shown in fig. 9 and their basal spacings in table 8. These diffractograms indicate that for all situations, there is an identical orientation of the amorphous phase, at a distance of 10.1 Å. The diffractograms indicate that for all the 4 micro-composites, regardless the value of molecular weight, the diffraction maximum for similar angles: 2.95 – 3.02 Å and 5.78 – 5.99 Å. In this case too, the height, the width and the area of diffraction peaks differ.

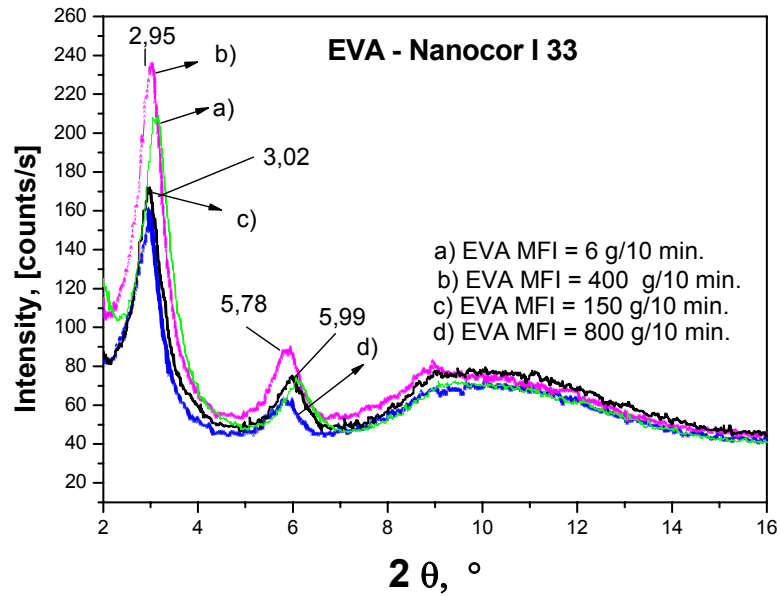


Fig. 9 – The X rays diffractograms of the microcomposites of EVA with different molecular weights and 3 % Nanocor I 33.

Table 8

The XRD basal spacing of the micro- composites of EVA with different molecular weights and 3 % Nanocor I 33

EVA MFI, g/10 min.	2 teta, °	d, Å
6	3.03;6.04;	33.8; 17;
150	2.98; 5.95;	34.4;17.2
400	2.96; 5.9;	34.7; 17.4
800	2.95; 5.89;	34.8; 17.4

Nanocor I 33 is relatively more homogenous than the other studied silicates, whereas the interbasic distance is by 30.29 – 30.6 Å (fig. 5, table 4). The micro-composites have a heterogeneous morphology because, nearby the main galleries of 33 – 34 Å, there are others of approx. 17 Å. Regardless the molecular weight, in

all the 4 studied micro-composites the basal spacings have approximately the same size of 33 – 34 Å, that means a galleries “swelling” with only 2 Å. This small galleries enlargement is a prove that the **dodecyl pyrrolidone** functionality of Nanocor I 33 are not compatible with the vinyl acetate groups from EVA.

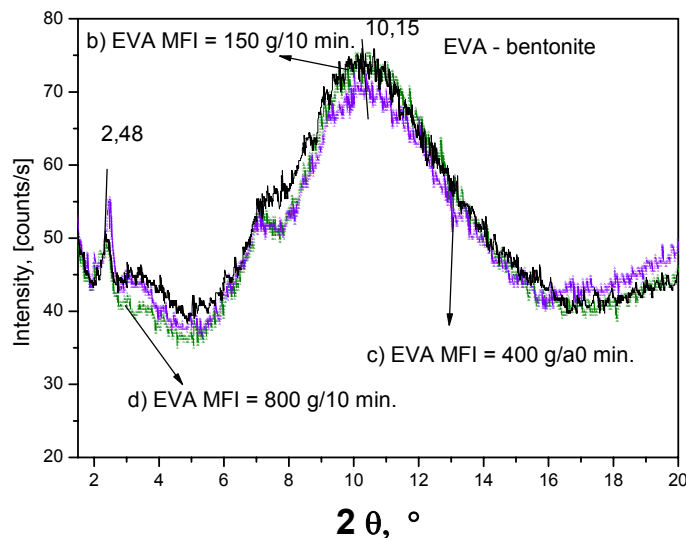


Fig. 10 – The X rays diffractograms of the microcomposites of EVA and 3% bentonite.

On the diffractograms of the micro-composites of EVA with bentonite (fig. 9) a very wide maximum at 10.15° with the intensity of 75 counts/s and other smaller at 2.48° with the intensity of 65 counts/s appears. Data from Table 9 proves that if EVA has MFI = 6 g/10 min., then at

the melt compounding with bentonite, a silicate enlargement from 12.43 \AA to 30 \AA , i.e. a swelling of $27 - 27 \text{ \AA}$ takes place. If the polymer molecular weight is smaller then, regardless the molecular weight, the bentonite galleries swelling is only by approx. 30 \AA .

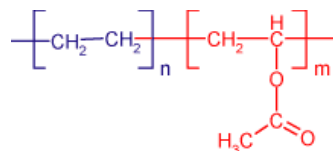
Table 9

The XRD basal spacing of the micro-composites of EVA and 3% Bentonite

EVA MFI, g/10 min.	2 teta, °	d, Å
6	8.4	30.2
150	2.35; 7;	43.6; 14.7
400	2.34; 3.37; 7.04;	43.8; 30.4; 14.6
800	2.44; 7;	42; 14.7

DISCUSSION

It is known that EVA is a statistical copolymer, based on ethylene and vinyl acetate (formula 3) which is obtained industrially by radical copolymerization at high pressure.¹³ The copolymer



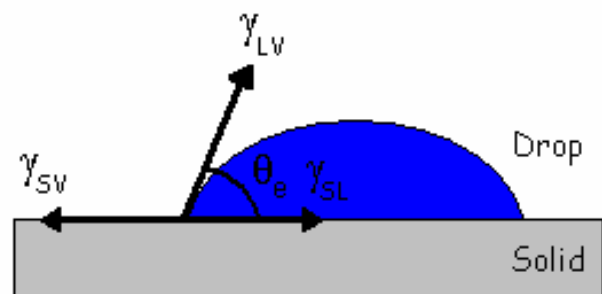
(formula 3)

In the performed experiments, EVA with 28% acetate groups was used. The obtained results showed that this type of EVA, better incorporated the non treated silicates. If the silicates were treated then the functional groups of ammonium type which contain small radicals more efficient are. Functionalizing of the silicate galleries with the pyrrolidion ions is not efficient. The explanation

of this result is connected to the predominant non-polar and hydrophobic character of EVA with 28 % polar groups in the molecular chains.

The molecular mass of EVA is another parameter which controls the polymer properties. The bigger the molecular weights, the higher the fluidity and the wettability are.

Fig. 11 – Graphic representation of the contact angle as an expression of liquid wettability (polymeric melt)¹⁴.



As it is known, the wettability is given by the value of contact angle between a liquid drop within the thermic equilibrium with an horizontal surface (fig. 11).¹⁴ If the wetting angle θ has a value lower than 90° then the fluid has good wetting properties. If the wetting angle is between 90° and 180° A then the fluid has bad wetting properties.

The thermodynamic wetting equilibrium depends on the interface tension and is defined by the formula 6.

$$0 \leq \theta \leq 90 \quad (\text{formula 4})$$

$$90 \leq \theta \leq 180 \quad (\text{formula 5})$$

$$\gamma_{s,v} = \gamma_{s,l} + \gamma_{l,v} \cos \theta \quad (\text{formula 6})$$

where: $\gamma_{s,v}$ represents the gas – solid interface tension, $\gamma_{s,l}$ is the solid – liquid interface tension and $\gamma_{l,v}$ the liquid – gas interface tension. Considering solid the silicate galleries and liquid the polymer melt, all the above-mentioned can explain the compatibility between the polymer melt and silicate galleries.

In all silicate – EVA pairs that differ through the molecular weights, it was noticed the same diffraction peaks, but depending on the molecular weight the peaks, have different height, width and specific area. The highest peaks were met in the cases of the biggest EVA molecular weight because of the higher wetting character of these macromolecular chains. The most eloquent situation was in the case of Nanocor I 28 when, for EVA with MFI = 6 g/10 min. the diffractogram didn't show any diffraction peak (fig. 8 a). All the above-mentioned results will be re-analysed from the TEM perspective coupled with the thermal analysis.

CONCLUSIONS

Some results concerning the obtaining of polymeric nanocomposites with improved barrier properties for food packaging based on melt processing techniques based on poly (ethylene–vinyl acetate) and layered silicates are presented. The study concerning the dependence between the polymer molecular weight and the silicate treatment on the EVA – layered silicates micro-composites morphology is detailed.

As a consequence of the wettability in proportion with the molecular weight values, the micro-composites with high morphological order level are obtained based on EVA with high molecular weight.

Because of the prevalent hydrophobicity of the EVA macromolecular chains with 28 % polar

groups, the biggest silicate “swelling” are obtained with un treated silicates. If the silicate was treated, then, between ammonium and pyrrolidion ions, the ammonium groups with the smaller substituents must be preferred. In case of big substituents the interactions with the vinyl – acetate group from EVA are weak and the silicate “swelling” unimportant

Because of the wettability in proportion with the molecular weight, EVA with higher molecular weight reinforced with multilayered silicate lead to the micro-composites with higher content of ordered phase. This dependence is more pronounced in the case of silicates with treated galleries which is more compatible with the polymer.

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