

NANOCOMPOSITES BASED ON COPOLYMER ETHYLENE AND VINYL ACETATE/CLAY WITH DIFFERENT TYPE OF NANOFILLER

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Abstract:

Nanocomposite materials with layered clay used as nanofiller and copolymer ethylene and vinylacetate matrix (EVA, the content of VA component 9 wt. %) were prepared by compounding the individual components in KO Buss kneader. The nanofiller MMT Na⁺, modified by EG and DEG by means of ion-dipole intercalate method, was used to evaluate ethyleneglycol (EG) and diethyleneglycol (DEG) as potential intercalantes for montmorillonite. For the purpose of organofilization, two different concentrations of the above-mentioned intercalate reagents were used. Moreover, two types of commercial products such as Nanofil N 5 and N3000 were used as other nanofillers. The quantity of all the above-mentioned nanofillers was 5 wt. % in relation to the content of montmorillonite. The level of intercalation of our nanofillers was evaluated by means of XRD method.

The morphology of nanocomposite EVA/clay samples was also examined by means of XRD analysis illustrated by light microscopy scans and transmission electronic microscopy TEM. Furthermore, mechanic properties such as DMA and tensile strength were observed. As these materials are widely used in packaging industry, our next attention was focused on the impact of the nanofiller on permeability of the prepared nanocomposite samples, namely permeability for oxygen, carbon dioxide and water vapour.

Despite the fact that the XRD and microscopy results have revealed that complete exfoliation did not take place in any case, mechanic properties as well as the permeability measurements show that nanofiller Nanofil 3000 might be suitable for the above-mentioned polymeric matrix.

Key words: nanocomposites, EVA copolymer, montmorillonite, permeability, ethyleneglycole, diethyleneglycole, intercalation

1. INTRODUCTION

In general, polymeric materials have played a significant role in packaging industry for quite some time. The use of bags and sacks of different properties has become routine in everyone's life. However, hardly anyone is aware of the large scale of requirements these polymeric packing materials have to satisfy in order to be used for the production of high-quality wrappings¹⁻³.

Generally speaking, the main function of a wrapper is to protect a product. It can be said that the vast majority of polymeric wrappers are used in the form of plastic films of different thickness. The actual requirements for a wrapper are always bound up with its final application or, in other words, the properties of the product or material it is supposed to protect. A relatively small scale of requirements has to be satisfied in case of products where the actual content is already protected in some way and these products have to be transported from one place to another. In this case, the most important quality to be

observed is the mechanical durability of the material which has to stand the strain of the manipulation⁴⁻⁶.

The scale of requirements for wrappings that are supposed to protect and be in direct contact with food, for example, is much larger. In this instance, the requirements concerning the durability of polymeric film are not sufficient as it is also necessary to satisfy various hygienic criteria such as the storage and preservation of food in its original condition for as long as possible. Most frequently, it is necessary to prevent oxygen from coming into contact with the wrapped food. This can be achieved either by using a material with low permeability for oxygen or by forming protective atmosphere around the food⁷. In case of protective atmosphere, for example N₂, CO₂ or a suitable mixture of gases⁸, it is necessary for the wrapping film to preserve the original chemical composition of the protective atmosphere for the entire storage period so that no gas molecules are released. These requirements, closely related to permeable qualities of materials, are fulfilled by some polymers, which are already being produced for this purpose (e.g. polyamide)⁹⁻¹¹. In order to improve their not very good mechanical qualities, PA films are combined with e.g. polyethylene films, which results in the production of multi-layer wrapping films¹⁰.

Polymeric nanocomposites are materials made up of a polymeric matrix where the particles of filler, distributed homogeneously, have at least one of their dimensions in nanoscale. These days, the most frequently studied examples are carbon nanotubes and layered clay minerals. They have a special quality – after the treatment by so-called organofilization and subsequent mixing with a polymer they break into nanoleaves, i.e. particles with a high aspect ratio and the thickness of about 1 nm. The materials prepared this way show a substantial improvement of many qualities such as e.g. modulus, fire resistance or gas permeability, with much lower loading (about 5 wt. %) in comparison with conventional nanofillers¹²⁻¹⁵. It is the significant reduction of gas permeability that gave rise to a deeper study of these nanocomposites, which might be suitable for the production of films for wrapping materials.

The most frequently used type of nanoclay is montmorillonite (MMT). It is a layered mineral belonging to a group of clay minerals with octahedral and tetrahedral nets in the ratio of 2:1. In order to increase its exfoliation in the polymeric matrix, it is modified by the process known as organofilization or intercalation, i.e. the insertion of a suitable organic compound into MMT interlayer¹⁶⁻¹⁸. This way, a broader d-spacing as well as reduction of gravitational forces between the individual platelets of montmorillonite are reached. Consequently, this leads to the reduction of energy needed for the breakup of nanofiller into the individual nanoleaves in the polymeric matrix after the process of compounding.

The preparation of nanocomposites with PE matrix or a matrix of a similar nature, such as the PE/vinylacetate copolymer, is more complex than e.g. in case of PA or PES nanocomposites. It is given by a different nature of both components, where MMT is highly polar while the polymeric matrix of the mentioned type is rather nonpolar. In case of PE it is necessary to add the so-called compatibilizer (e.g. maleic PE or PP)¹⁹⁻²². As far as EVA copolymer matrix is concerned, the problem is partially solved by adding a certain amount of a more polar vinylacetate compound.

The aim of the presented paper was to examine the possibilities for the preparation of nanocomposite materials with ethylene/vinylacetate copolymer matrix and the evaluation of their properties. From the point of view of intercalation, ethyleneglycol and diethyleneglycol were evaluated as potential intercalantes for PE nanocomposites. Regarding the conceivable use of this material in packaging technology, the permeability for selected gases has also been assessed.

2. EXPERIMENTAL

The preparation of test samples

Cloisite®Na⁺ intercalation

Because of the polarity difference between the polymeric matrix and montmorillonite (MMT), it is necessary to change hydrophilic montmorillonite into organophilic montmorillonite. MMT was modified by ethyleneglycol (EG) and diethyleneglycol (DEG) with

the concentration of MMT : EG (DEG respectively) 1 : 1 and 2 : 1. The intercalantes were prepared by the process of mixing in the rotary Thermomix blender at the temperature of 80°C for 20 minutes.

As another nanofiller, N5 and N3000 Nanofil from Sudchemie, Germany were used. The quantity of all the above-mentioned nanofillers added to the polymeric matrix was 5 wt. % in relation to the content of MMT. The characteristics of the individual nanofillers are summarized in Table 1.

Table 1. The characterization of nanofillers

Nanofiller	Medium particle size	Intercalant	D-spacing
Nanofil® 5	8 µm	distearyldimethylamoniumchlorid	2,8 nm
Nanofil® SE 3000	10 µm	-	-
Cloisite® Na ⁺	2 µm < 10% 6 µm < 50% 13 µm < 90%	-	1,25 nm

Copolymer matrix used: EVA copolymer – GREENFLEX FF 35 (VA content 9 wt. %, melt index 0.7, density 0.92 g/m³), from Polimery Europa

Mixture blending

EVA mixtures with nanofillers were blended in one-screw extrusive KO BUSS machine at the temperature of 150°C, rpm 280 min⁻¹. The process took place in Fatra Napajedla company.

The homogenized matter came out of an extrusive dye into a cooling bath in the form of a string and was subsequently granulated.

The prepared granular was used for pressing plates. The pressing took place at the temperature of 200°C. For the purpose of tensile strength test, bodies with a blade on either side were cut out from these plates. There were 12 bodies prepared for each mixture. The same bodies were used for the preparation of samples for TEM, LM, DMA and XRD tests.

Film pressing

The next task for our experiment was to extrude films of the thickness of 0.05 mm for the measurement of barrier properties. The films were extruded on a pre-arranged assembly line consisting of the following parts: an extrusive screw Brabender machine, a special extrusive wide-slot dye, a cooling cylinder and a reel. The thickness of the film was regulated by the speed of the pullout on the one hand and cooling of the cylinder by an electric pump on the other.

Evaluation of the samples prepared

X-ray diffraction analysis

X-ray diffraction analysis was performed on URD 6 diffractometer in FT UTB, Zlín. The measurements were made in the reflective mood in the range of 2Θ counting for 2-30° with a step of 0.02 for the evaluation of both powdered nanofillers and polymeric nanocomposites of our own production.

Light microscopy

The whole plates (of the thickness of about 2mm) in the transmitted light were used as samples. The shots were taken by means of SMZ-2T stereomicroscope and a digital camera DXM 1200 (Nikon).

Transmission electronic microscopy

For the purpose of TEM, ultra-thin cross-sections prepared on a special cutting device LEICA ULTRACUT UCT ultracryomicrotome at the temperature of -110°C were used. TEM was performed on a JEM 200CX (JEOL) device at 100 kV. The scans taken were digitised by means of a computer-controlled digital camera DXM1200 (Nikon).

Dynamic mechanical analysis

The dynamic mechanical analysis was performed on a DMA DX04T device (R.M.I., Czech Republic – FT UTB Zlín). The samples for this test had been prepared by means of pressing. DMA was performed at the temperature of 30°C.

Tensile strength test

The tensile strength test was performed on a T 2000 Alpha technologies device. The test samples were in the shape of bodies with a blade on either side. These had been cut out

from the pressed plates. The speed of jaw shift was set on the value of 25 mm per min and the initial distance between the jaws was 60 mm. The test was carried out until the rupture of the tested bodies. For each mixture 10 measurements, out of which the arithmetic means are given, have been taken.

Barrier properties

Blown films with the thickness 0,05 mm were tested. The permeability for oxygen and carbon dioxide was carried out on the device for gas permeability with a pressure pickup LMP 150 (made in Tesla Rožnov, Czech Republic), at the temperature 25°C and the hypertension 0,4 – 0,6 MPa.

3. RESULTS AND DISCUSSION

XRD. In order to discover the result of intercalation of montmorillonite by means of ethyleneglycol and diethyleneglycol, XRD patterns, summarized in Fig. 1, have been taken. According to the recorded results it is possible to observe peak shifts towards broader d-spacings, however, this increase is not significant. It can also be said that no regular molecule arrangement of the EG and DEG organic compounds within the MMT interlayers took place. The X-ray diffraction analysis of EVA (9 % VA) copolymer was performed in order to evaluate the achieved level of exfoliation of nanofiller particles in EVA matrix. In the following graph (Fig.2) the XRD patterns of EVA mixtures with 5% loading are shown.

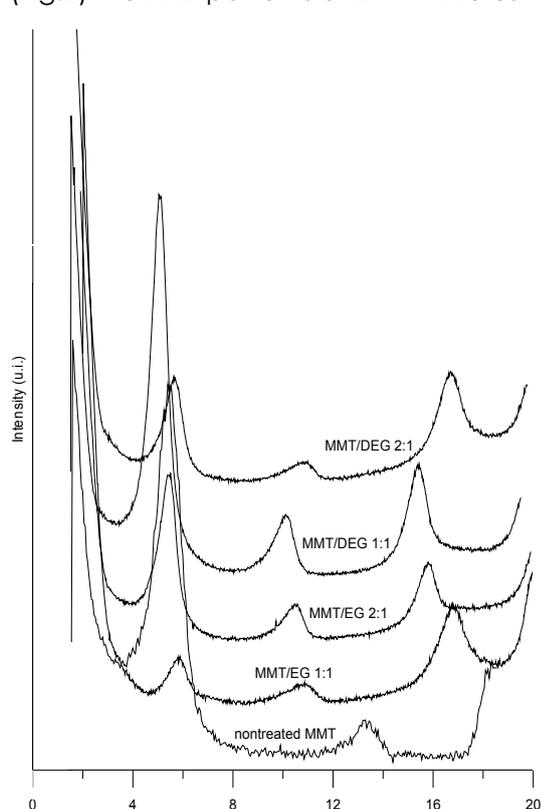


Figure 1 XRD patterns of treated MMT by EG and DEG with different ratio

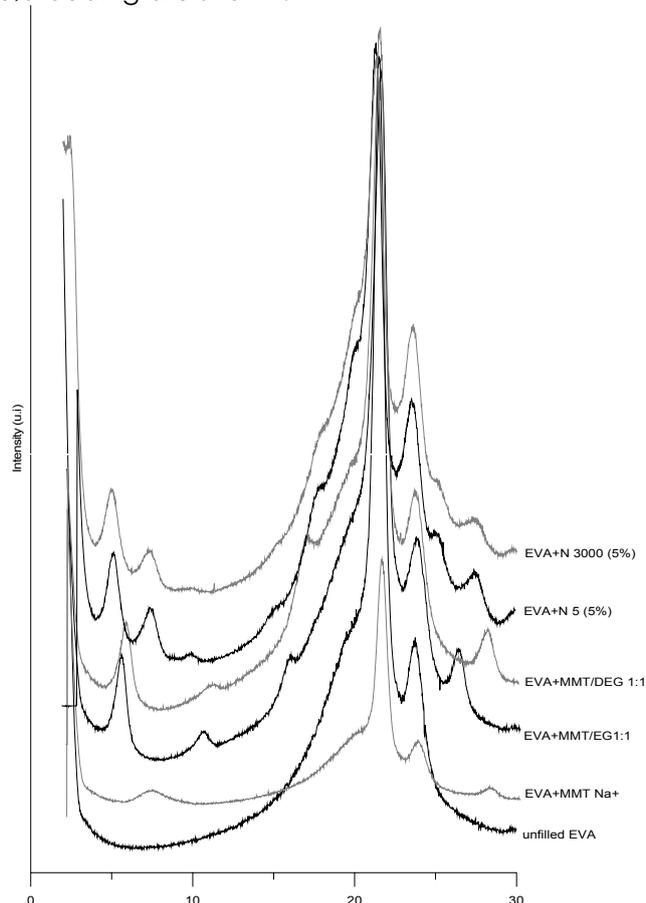


Figure 2 XRD patterns of EVA/nanofiller nanocomposites with 5% loading

Unfortunately, according to the patterns summarized in Fig. 2 it cannot be said that complete exfoliation has taken place. It is possible to see the difference between the unfilled EVA copolymer and the loaded copolymer. All of the samples observed exhibit peaks around 7°, which correspond to MMT. As for this graph, it is necessary to note that the XRD patterns of the samples loaded with N5 and N3000 are recorded from 3° upwards. In this case, it has no impact on the evaluation of the level of intercalation, however. As discussed below, despite

the incomplete exfoliation shown by XRD measurement, a certain improvement of some qualities observed has taken place.

Light microscopy. LM was used to evaluate the morphology of the samples prepared. Fig. 3 and 4 show the scan samples of EVA and MMT base, which had been treated by EG and DEG with the ratio of 2:1. As mentioned in case of XRD patterns of these samples, a significant increase of d-spacings did not take place and this was also reflected in the LM measurement. It is quite evident that neither complete homogenization nor the exfoliation of nanofiller in EVA matrix has taken place. The dark spots in the scans represent particles of non homogenous nanofiller. The situation is better in case of the used ethyleneglycol intercalante (left) than in case of the used diethyleneglycol (right). As this scan shows, there is still a certain amount of unbroken particles in the sample. This might cause deterioration of mechanical qualities, which is discussed below.

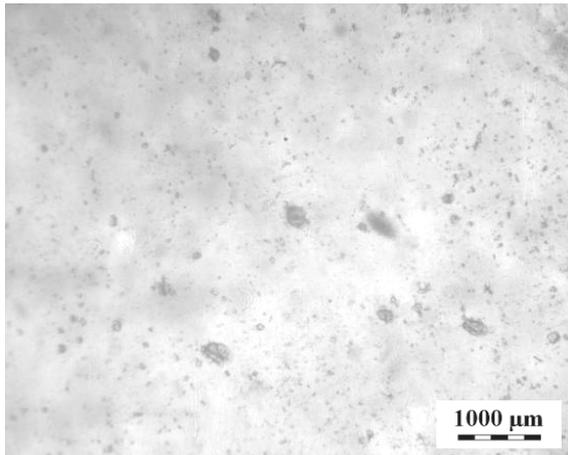


Fig. 3. LM picture of the sample EVA + MMT/EG 2:1

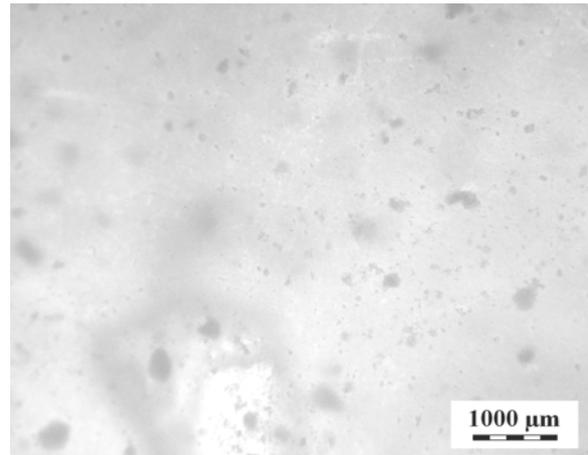


Fig. 4. LM picture of the sample EVA + MMT/DEG 2:1

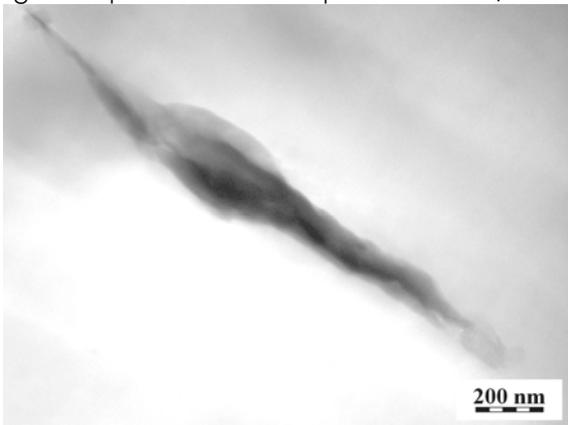


Fig. 5. TEM picture of the sample EVA + MMT/EG 2:1

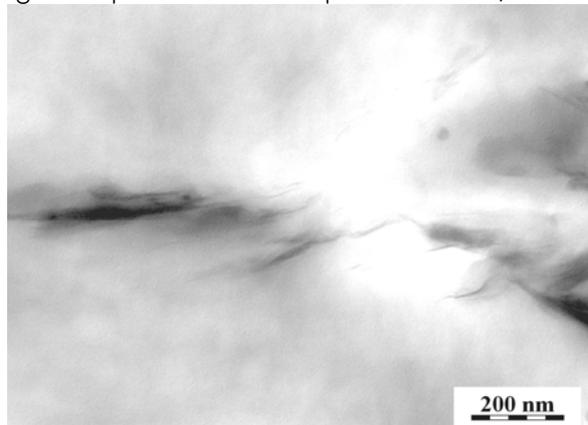


Fig. 6. TEM picture of the sample EVA + N 3000

TEM. TEM was used in order to complete the information about morphology of the samples that did not show any dark spots representing non exfoliated nanofiller when examined by means of LM. Fig. 5 and 6 compare TEM scans of EVA samples loaded by MMT/EG in the ratio of 2:1 with N3000 under the same magnification. In case of MMT/EG, it can be said that in the polymeric matrix there are particles with the thickness of more than 100nm, thus none in the scale of the individual MMT platelet. As far as the second scan is concerned, i.e. the one showing the sample with commercially produced nanofiller suitable for this type of polymeric matrix, a higher level of exfoliation took place here. In comparison with the previous scan, here it is possible to observe particles of the thickness of only about 40 nm despite the fact that they are not completely exfoliated. Next to them, it is possible to see darker lines in a lighter polymeric matrix, which represent the individual MMT platelets. Later on this result will be discussed in relation to other properties observed.

DMA. The aim of the measurement was to assess the dynamic elasticity modulus E^* and also the loss angle δ . The recorded values of DMA are summarized in Table II.

Table II. DMA data of EVA/nanofiller nanocomposites

GF1	[E*] Mpa	tg δ
GF1 cista	126,22	0,1615
MMT/EG 1:1	115,31	0,1901
MMT/EG 2:1	132,49	0,1809
MMT/DEG 1:1	114,01	0,1876
MMT/DEG 2:1	131,58	0,1854
N 3000 (5%)	238,02	0,1620
N5(5%)	273,19	0,1579
Na+ 5%	135,41	0,1824

Fig. 7 illustrates the data of the dynamic E* modulus. It is evident that almost all composites prepared show an increased dynamic elasticity modulus. A significant increase took place in case of the sample filled by Nanofil 5, where the value of E* increased by more than 120%. It is followed by the sample filled by Nanofil 3000, where the value increased by 90%.

Further measurements related to the loss angle δ. The results are summarized in a graph in Fig. 8. In this case, the improvement of all samples has also taken place, however, in comparison with the E* modulus values, the differences between the individual values are not so marked. This could be explained by different significance of the two quantities.

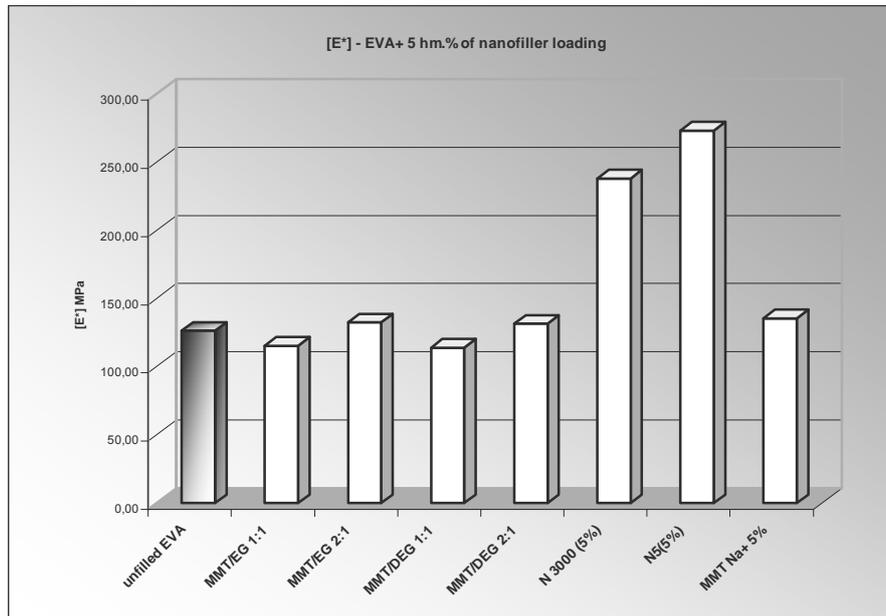


Fig 7 E* modulus for EVA nanocomposites filled by 5 % of nanofiller

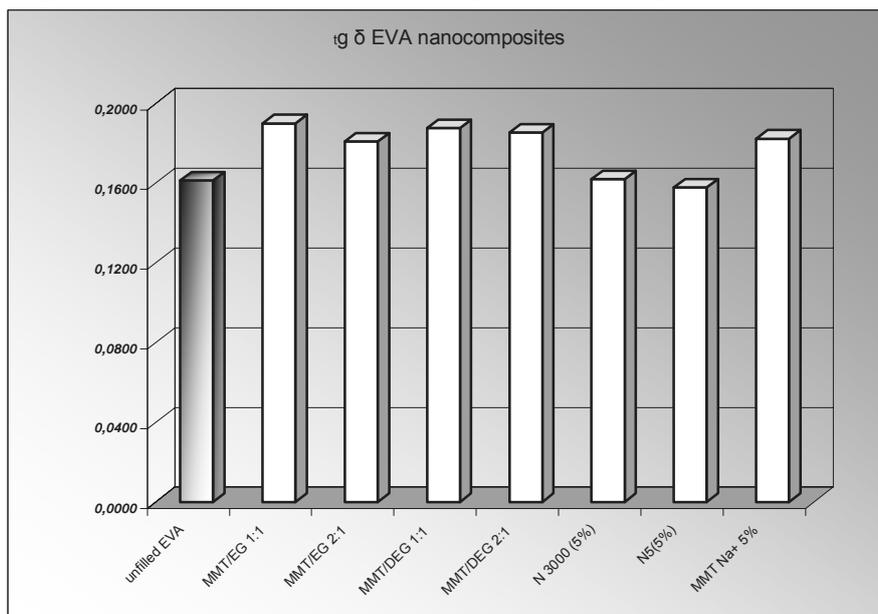


Fig 8 Data of tg δ for EVA nanocomposites filled by 5 % of nanofiller

Mechanical properties. From the values observed, the results of tensile strength, upper yield stress and tensility were gained by measuring the qualities of the sample bodies made by means of pressing and subsequent cutting out. The recorded values are arithmetic means of ten measurements (See Table III).

Table III. Values of the mechanical properties

	Tensile strength (MPa)	Elongation (%)	Yield stress (MPa)
Unfilled EVA	16,102	616,565	6,923
MMT/EG 1:1 (5%)	10,978	512,030	6,487
MMT/EG 2:1 (5%)	6,198	366,150	6,559
MMT/DEG 1:1 (5%)	11,222	555,420	6,322
MMT/DEG 2:1 (5%)	12,180	553,450	6,594
N 5 (5%)	8,147	441,225	7,204
N 3000 (5%)	14,373	614,080	7,128
MMT Na ⁺ (5%)	14,103	599,716	7,024

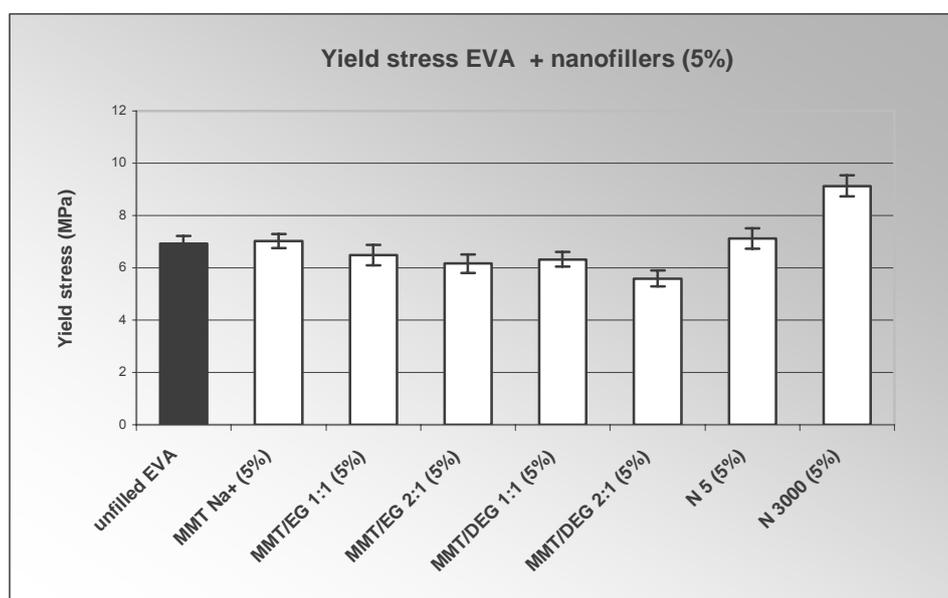


Fig 9 Yield stress of EVA/nanofiller samples filled by 5% of nanofiller

The first quantity is again the upper yield stress (see Fig. 9). An interesting result appears to be the upper yield stress value of EVA copolymer filled by unmodified montmorillonite, where the value is slightly higher in comparison with both unfilled EVA copolymer and the fillers of our own production. An increased upper yield stress can be observed in case of Nanofil 5 and mainly in case of Nanofil 3000. At the same time, all the fillers of our own production show a slight decrease in the upper yield stress, which might be caused by incomplete homogenization confirmed by LM scans.

Unfortunately, according to Fig. 10 it cannot be said that the values of tensile strength have increased in any way, conversely, they have decreased in case of all samples. The lowest values of all have been reached by EVA copolymer filled by our MMT/EG filler in the ratio of 2:1, which is confirmed by the above-mentioned LM scan (see Fig. 10). On the other hand, the best results can be observed in case of Nanofil 3000 but again, when compared with the unfilled copolymer, the tensile strength values are lower. It is interesting to note that the copolymer filled by unmodified MMT Na⁺ shows better tensile strength qualities than the copolymer filled by modified MMT. This observation can be explained by the fact that tensile strength might be influenced by incomplete exfoliation of MMT particles, where its bigger agglomerates work as a potential source of disconnection during the tension in matrix. This also corresponds to relatively big differences between the individual values, out of which the arithmetic mean shown in the graph has been calculated.

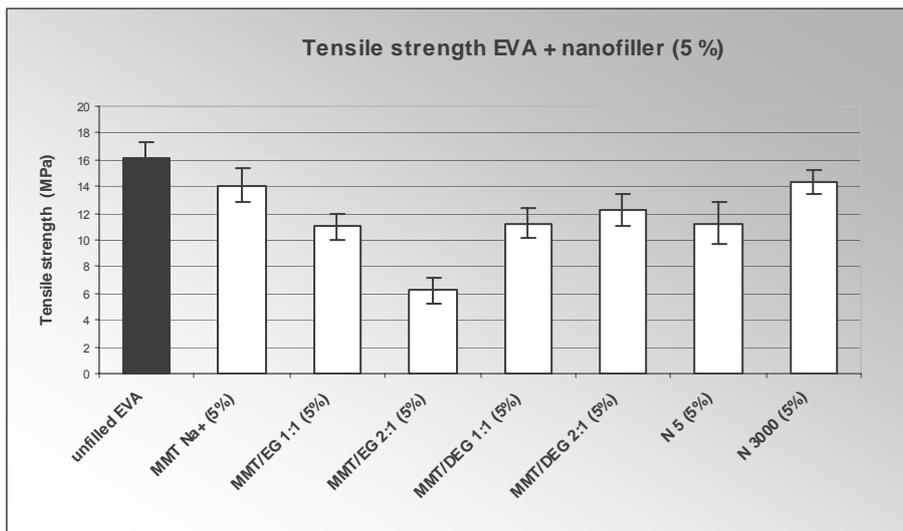


Fig 10 Tensile strength of EVA/nanofiller samples filled by 5% of nanofiller

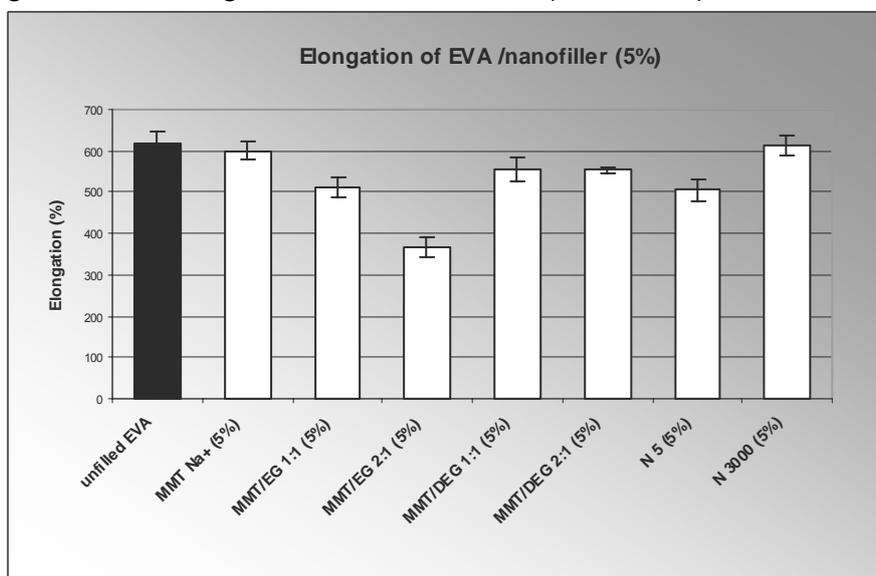


Fig 11 Elongation of EVA/nanofiller samples filled by 5% of nanofiller

Also, when evaluating the elongation of the filled EVA copolymer (Fig. 11), there is no improvement in comparison with the unfilled copolymer. Again, the least effective seems to be, as in case of tensile strength, the copolymer filled by MMT/EG 2:1. Another rather unsuitable filler is Nanofil 5, which shows even lower values than the intercalantes of our own production. Again, the best results have been recorded in case of Nanofil 3000, where the values of elongation are almost identical to those of the unfilled copolymer; however, no improvement has taken place either.

Permeability. As mentioned above, EVA copolymer is one of the polymers used in packing industry. Therefore, our study also covers the values of permeability for oxygen and carbon dioxide, which are gases that should be prevented from penetrating through film, e.g. in case of food wrapping.

In this instance, films extruded on a flat extrusive dye were used as samples for the purpose of measurement.

Fig. 12 summarizes the values of oxygen permeability coefficient. The resultant values of the individual samples vary to a large extent. A decrease in permeability has taken place in case of EVA + MMT/EG 1:1 and Nanofil 3000, namely by about 20%. On the other hand, the value of EVA/Nanofil 5 coefficient has increased more than 5 times.

The results of measurement of the same coefficient for carbon dioxide are remarkably different. In case of EVA/Nanofil 3000 sample, reduced permeability was observed similar to that for oxygen. Unlike the previous result, however, the permeability for CO₂ in case of EVA/Nanofil 5 decreased as well. Moreover, its value was even lower than the one for N 3000. The worst results were recorded for the systems containing MMT with a higher ratio, i.e. the ones modified by ourselves. These differences might be caused by dissimilar nature and behavior of the molecules of both gasses tested.

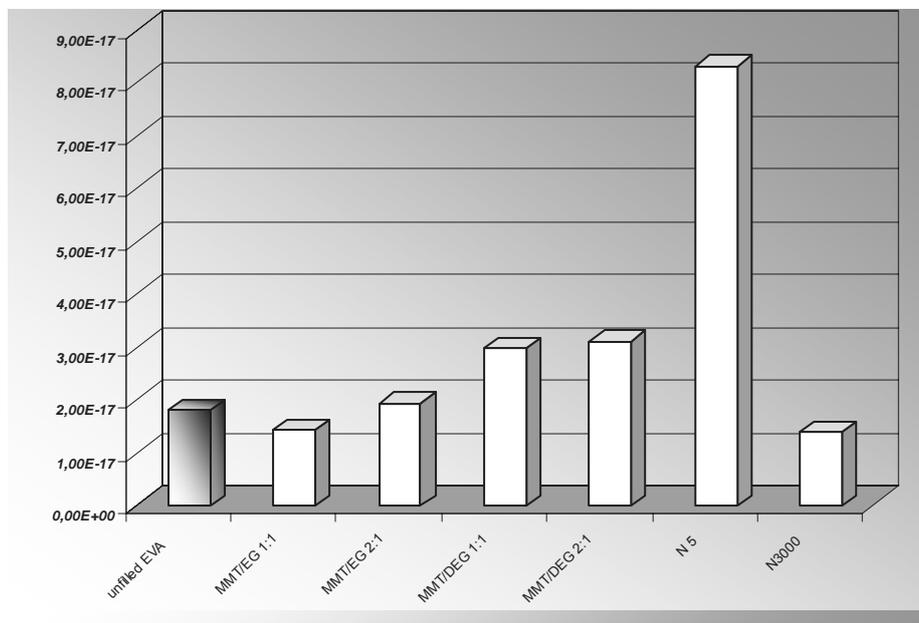


Fig 12 Oxygen permeability coefficient of EVA/nanofiller samples filled by 5% of nanofiller

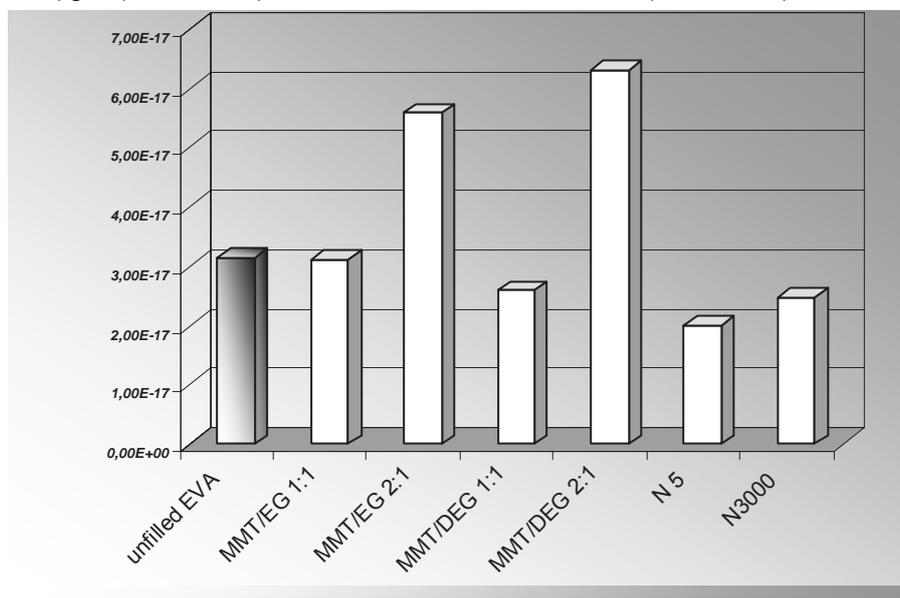


Fig 13 Carbon dioxide permeability coefficient of EVA/nanofiller samples filled by 5% of nanofiller

4. CONCLUSION

Nanocomposites with the polymeric matrix of EVA copolymer were prepared. MMT modified by ourselves by means of ethyleneglycol and diethyleneglycol in the ratio of 1:1 and 2:1 respectively was used as nanofiller. These systems were employed for the evaluation of their potential use as intercalantes in the polymeric matrix observed. It has been found out that under the conditions needed for their intercalation, neither significant increase of the interlayer spacing nor exfoliation during subsequent compounding with EVA took place.

Furthermore, two commercial products such as Nanofil 5 and 3000 were used as other nanofillers.

Morphology evaluation of the samples prepared has proven that sufficient exfoliation of MMT/EG;DEG fillers did not take place and moreover, further qualities observed have not shown a dramatic improvement of samples with the above-mentioned nanofillers.

The commercial samples of nanofillers, which are labelled by the producer as suitable for the polymeric matrix observed, have shown better results. Despite the fact that neither XRD nor TEM proved complete exfoliation of MMT particles, the samples with Nanofil have caused a substantial improvement of both mechanical and permeability qualities.

In conclusion, it can be said that neither ethyleneglycol nor diethyleneglycol are organic substances to be used as suitable intercalantes for EVA polymeric matrix and, conversely, the use of Nanofil 3000 seems to be suitable for this purpose. Further research will be focused on the study of different compounding conditions as well as a different compounding device for the purpose of improving the qualities observed.

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