

Barrier properties of polymer/clay nanocomposites

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ABSTRAKT

Polymer/jílové nanokompozity se v posledním desetiletí řadí mezi nově vznikající materiály. Jíly jsou používány jako plnivo především díky jejich dostupnosti a dobrým vlastnostem. Jílové minerály již při nízkém obsahu plniva zlepšují bariérové a mechanické vlastnosti. Tato práce je zaměřena na studium polymer/jílových nanokompozitů s použitím PVC jako polymerní matrice. Ačkoliv tento polymer má sám o sobě dobré bariérové vlastnosti, je nezbytné zkoušet plnění novými typy plniv ke zlepšení aplikačních vlastností. Navíc má PVC své uplatnění jako střešní fólie a ostatní vodovzdorné fólie nebo balící materiály, kde jsou bariérové vlastnosti velmi důležitou charakteristikou pro průmyslové využití. Cílem této práce bylo srovnání bariérových vlastností v závislosti na použitém typu MMT (Cloisite Na⁺, Cloisite 30B) a poměru ko- a interkalačních činidel a zároveň nalezení materiálu s nízkou permeabilitou par, vysokou odolností vůči rozpouštědlům a samozřejmě nízkou cenou. Metody použité k interpretaci výsledků srovnávají vlastnosti námi připravených vzorků s komerčně vyráběnými izolačními foliemi.

ABSTRACT

Polymer/clay nanocomposites are a new class of emerging materials in the last decades. Clays are used as filler due to their availability and good properties. In the low content of filler they improve barrier and mechanical properties. This Master thesis is oriented on the research of polymer/clay nanocomposite using PVC as polymer matrix. Although this polymer has good barrier properties as a raw material, it is necessary try to fill it by new types of fillers to improve properties in applications. Furthermore, this polymer can be applied as roof films and other waterproof films or packaging materials, where barrier properties are very important for characterisation of material into industry utilization. The aim of this work was comparing barrier properties in dependence on using type of MMT (Cloisite Na⁺, Cloisite 30B) and ratio of co- and intercalation agents and come up with materials that have low permeability to vapours, high solvent resistance and low cost as inherent characteristics. The methods for the interpretation of the result proposed in this study consider comparing our prepared samples with commercially insulation membranes.

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I declare I worked on this Master Thesis by myself and I have mentioned all the use literature.

Zlin, 10th May 2007

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Signature

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INTRODUCTION

The reinforcement of polymers using fillers, whether inorganic or organic, is common in the production of modern plastics. Fillers play important roles in modifying properties of polymers and reducing the cost of their components.

Lately, one of the most developing branches has been nanotechnology, which concentrates on both making and utilization of inorganic nanoparticles of different types, e. g. carbon, clay, silicates, ceramics and other materials.

Polymer nanocomposites are a new class of materials. Their originality, compared with conventional composites, consists in using filler with at least one of dimensions in the nanometer range. A potential nanoscale additive is a clay mineral because of its compressed silicate layers in which the fundamental unit is 1 nm thin planar structure. Moreover, clays create much higher surface area for polymer/filler interaction as compared to conventional composites.

Clay particles can provide large improvements of material properties by low filler content (less than 5%) in the polymer matrix. Thus, these materials can have many potential applications, such as packing films.

Barrier properties of PVC/clay nanocomposites have not been studied yet. Authors Ulutan and Balköse¹ deal with diffusivity, solubility and permeability of water vapour in flexible PVC/silica composites to improve these characteristics as a leather substitute. However, in our case we could achieve opposite result to practically use our materials as insulation membranes.

¹ ULUTAN and BALKÖSE. *Diffusivity, solubility and permeability of water vapour in flexible PVC/silica composite membranes*. Journal of Membrane Science 115 (1996) 217-224

I. THEORETICAL PART

1 POLYMER/CLAY NANOCOMPOSITES

In contrast to virgin polymers or to conventional composites, polymer/clay nanocomposites (PCN) are an important class of emerging nanocomposites. These materials have demonstrated significantly enhanced properties in a number of areas [1].

PCN have their origin in the pioneering research conducted at Toyota Central Research Laboratories, where these two divergent organic and mineral materials were successfully integrated. Fittingly, the first practical application of a nanocomposite was in the use of a nylon-montmorillonite clay nanocomposite as a timing belt cover on a Toyota Camry automobile [2].

1.1 Types of PCN

Depending on the interfacial interactions between the polymer matrix and layered silicate (modified or not), polymer/clay composites can be divided into four general types:

- *conventional composite* - the clay acts as a convention filler,
- *intercalated nanocomposite* - consisting of a regular insertion of the polymer in between the clay layers (called d-spacing),
- *exfoliated nanocomposite* - 1 nm-thick layers are dispersed in the matrix forming a monolithic structure on the microscale.
- *flocculated nanocomposite* - conceptually the same as intercalated nanocomposites. However, silicate layers are sometimes flocculated due to hydroxylated edge-edge interaction of the silicate layer [3].

Three types of composites can be seen in Fig. 1.



Fig. 1 Polymer/clay nanocomposites [1]

In an exfoliated structure, individual silicate sheets lose their layered geometry as a result of delamination, and dispersed as nanoscale platelets in a polymer matrix (Fig. 1). However, fully exfoliated structure is rarely seen in practice. An exfoliated structure is an idealized reference morphology that arises from only looking at local scale. In reality, the morphology is mixed intercalated/exfoliated structure [4].

X-ray diffraction (XRD) is commonly used for the characterization of the structure of nanocomposites. The X-ray diffraction pattern in many cases can be deceptive in determining the level of intercalation/exfoliation. Disordered systems could mimic the pattern of an exfoliated system. The only reliable technique for establishing the extent of exfoliation in nanocomposites is transmission electron microscopy (TEM) [5].

1.2 Preparation of PCN

PCN can be manufactured in several steps.

1.2.1 Organophilization

The first step in the preparation of PCN is organophilization in other words intercalation, because most polymers are hydrophobic and are not compatible with hydrophilic clays. In this case, pre-treatment of either the clays or the polymers is necessary. Therefore a compatibilizing agent can be used, which is molecule constituted of one hydrophilic function (which likes polar media - clay) and one organophilic function (which likes organic molecules - polymer) [3].

Organophilization can be based on:

1. Ion-exchange reaction (Fig. 2) - original exchangeable cations in the interlayer space is replaced by suitable types of cations (inorganic, organic) in a water solution [6]. The most common exchangeable cations are Na^+ , Ca^{2+} , Mg^{2+} , H^+ , K^+ , and NH_4^+ . Alkylammonium ions (i.e. compatibilizing agent) are utilized here because they can be exchanged easily with the ions situated between the clay layers. Consequently, alkylammonium ions permit to lower the surface energy of the clay so that organic species with different polarities can be intercalated between the clay layers. However, amino acids or tetra organic phosphonium salts are also used to convert the clay surface from hydrophilic to organophilic. For given clay, the maximum amount of cations that can be taken up is constant and is known as the cation-

exchange capacity (CEC) [3]. The disadvantage of this interaction is production salt on the surface of product. For this reason washing of products is necessary at the end of reaction.

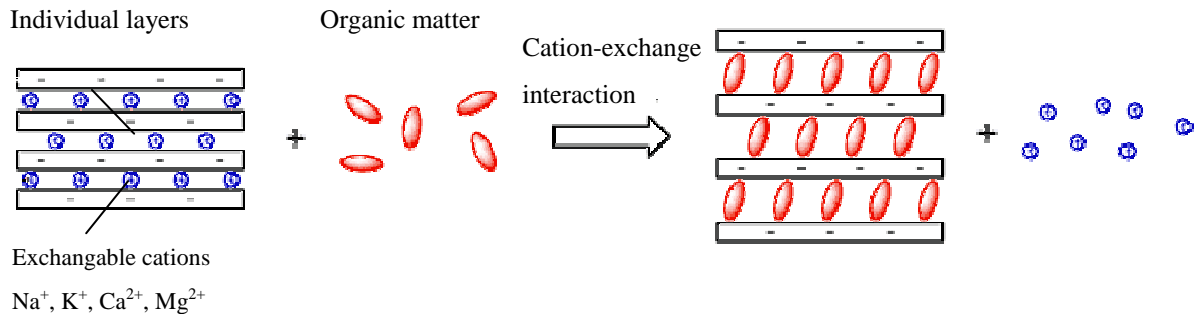


Fig. 2 Ion-exchange intercalation [3]

2. Ion–dipole interaction (Fig. 3) - original exchangeable cations remain in the inter-layer space and polar neutral molecules are intercalated into interlayer space between silicate layers [6] in solution even in melt of relevant intercalation agent. A classic example is water of hydration in many compounds. The complex has a definite ratio of organic or polymer to clay.

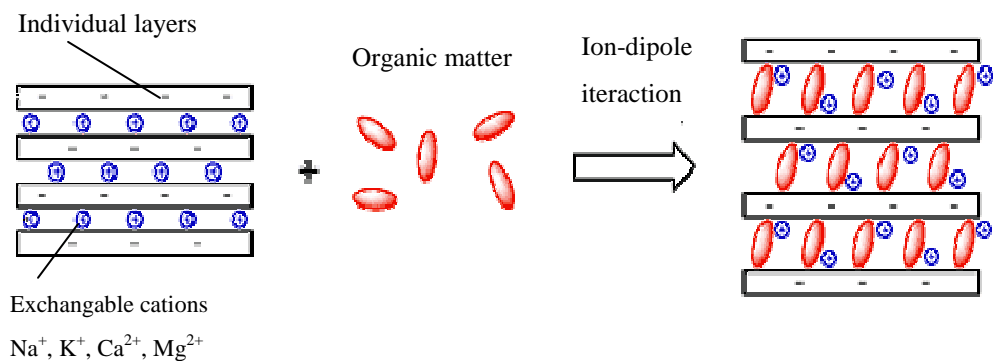


Fig. 3 Ion-dipole intercalation [3]

Moreover, these two interactions can be combined by co-intercalation of organic cations and polar neutral molecules into silicates. The choice of cations and molecules for intercalation is usually directed to the development of new interesting materials with beneficial properties for application in industry [6]. The reason for utilization of co-intercalation is degradation of some polymers (in this case PVC) by using intercalation agents with amino groups. Co-intercalation agents allow us decreasing the amount of amine in the composition and therefore lower the degradation process. In view this

fact, intercalation agent with –OH group and phosphate co-intercalation agents were used in this Master Thesis.

1.2.2 Synthesis of polymer/clay nanocomposites

The preparation of PCN itself can be realized through these four main methods:

In- situ polymerization

In-situ polymerization was the first method used to synthesize polymer-clay nanocomposites based on polyamide 6. As can be seen in Figure 4, this method involves inserting a polymer precursor (monomer in most cases) between clay layers and then their expanding and dispersion into the matrix by polymerization. Polymerization can be initiated either by heat or radiation, by the diffusion of suitable initiator or by an organic initiator or catalyst. The catalyst is fixed through cationic exchange inside the interlayer before the swelling of step. This method is capable of producing well-exfoliated nanocomposites and has been applied to a wide range of polymer systems [1, 7, 8]. PCN using following polymers were prepared by this method: PA 6, PE, PET, PP and epoxy resin [1].

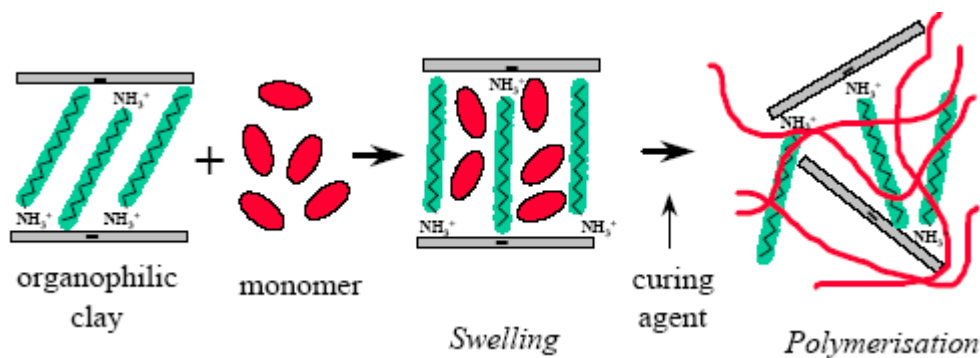


Fig. 4 The in-situ polymerization [3]

Solution-induced intercalation

The solution-induced intercalation method applies solvents to swell and disperse clays into a polymer solution. The layered silicate is exfoliated into single layers using a solvent in which the polymer is soluble. It is well known that layered silicates, owing the weak intermolecular forces that stack the layers together, can be easily dispersed in an adequate solvent. The polymer then adsorbs onto the delaminated sheets and when the solvent is evaporated, the sheets are reassembled, sandwiching the polymer to form, in the best case, an

ordered multilayer structure. The major advantage of this method is that it offers possibilities for the synthesis of intercalated nanocomposites based on polymers with low or even no polarity. Water-soluble polymers, such as PEO, poly(vinyl acetate), poly(2-vinyl pyridine) and ethylene vinyl acetate copolymer, have been intercalated into the clay galleries using this method. Examples from non-aqueous solvents are nanocomposites of poly(ϵ -caprolactone)/clay and poly(lactide)/clay in chloroform as a co-solvent, and high-density polyethylene with mixture of xylene and benzonitrile [1].

Melt intercalation

Figure 5 shows the melt intercalation process. As can be seen, the layered silicate is mixed with the polymer matrix in the molten state. Under these conditions and if the layer surfaces are sufficiently compatible with the chosen polymer, the polymer can crawl into the interlayer space and form either an intercalated or an exfoliated nanocomposite. So, no solvent is required. The approach can be applied in the polymer processing industry in order to produce nanocomposites based on traditional polymer processing techniques, such as extrusion and injection moulding [1, 3, 4, 8]. Nanocomposites containing different polymer matrices (PE, PP, poly(etherimide), PS) have been prepared by this method [1]. The melt intercalation method allows the use of polymers which were previously not suitable for in situ polymerization or solution intercalation. This method is the most common because neither a suitable monomer nor a compatible polymer-silicate solvent system is always obtainable.

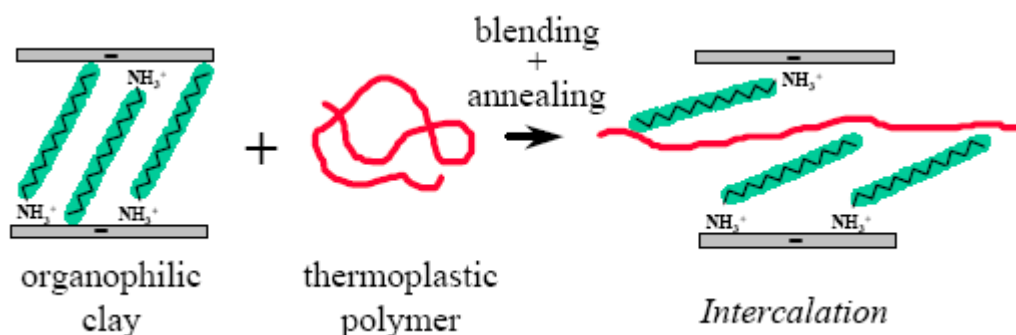


Fig. 5 The melt intercalation process [3]

Template synthesis

This technique, in which the silicates are formed in situ in an aqueous solution containing the polymer and the silicate building blocks, has been widely used for the synthesis of double-layer hydroxide-based nanocomposites. Unfortunately, it is far less developed for layered silicates. In this technique, based on self-assembly forces, the polymer aids the nucleation growth of the inorganic host crystals and is got trapped within the growing layers [7].

In addition to these major processing methods, other fabrication techniques have been also developed, for example, solid intercalation, vulcanization, and the sol-gel method. Some of these methods are in the early stages of development and have not yet been widely applied.

1.3 Characteristics of PCN

Nanocomposites consisting of polymer and clay frequently demonstrated improved mechanical and other material properties when compared to those of virgin polymer or conventional filler-reinforcement systems. Among enhancement properties belong chemical resistance, flame retardancy, thermal and dimensional stability and moreover decreasing permeability of gases and vapour. The last item will be discussed in these Master Thesis.

2 CHARACTERIZATION OF MATERIALS

2.1 Polyvinyl chloride

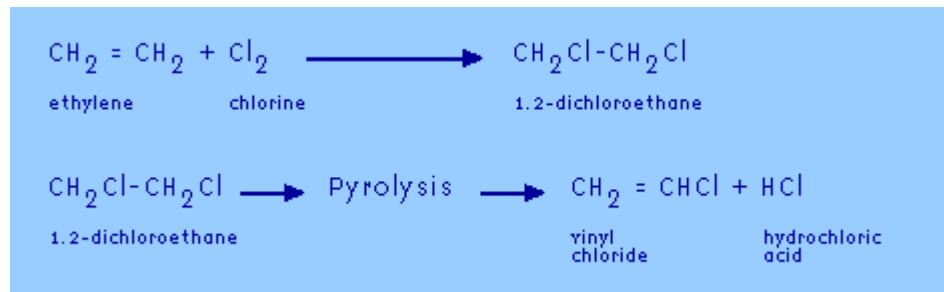
The first attempt to polymerise of vinyl chloride was reported in 1872 by Baumann [9]. However polyvinyl chloride (PVC) became well known only during World War II, when it substituted natural rubber for wire insulation and for waterproof sheeting. At present, there are still questions about health and safety aspects such as toxicity of stabilizers and plasticizers. Nevertheless, PVC belongs to the most produced polymers such as polyethylene and polypropylene.

2.1.1 Preparation of PVC

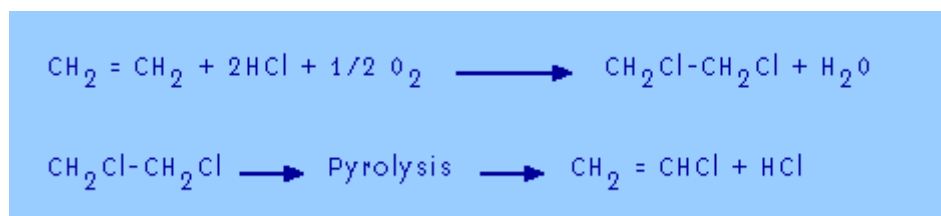
The monomer for the preparation of PVC is gaseous vinyl chloride ($CH_2 = CHCl$) in other words monochloroethylene.

The vinyl chloride can be manufactured in two ways [10]:

1. Chlorinating of ethylene and pyrolysis of the resulting 1,2-dichloroethane



2. Oxychlorination of the ethylene with the hydrochloric acid obtained during the preceding reaction, in the presence of oxygen, followed by pyrolysis of the resulting 1,2-dichloroethane



In the industry free radical polymerization is usually utilized. It can be carried out:

- in suspension
- in microsuspension
- in emulsion
- in block

The most often used is polymerization in suspension.

2.1.2 Properties of PVC

The produced PVC is a white powder with thermoplastic characteristics. It has unsuitable flowing properties and low thermal stability which cause difficult processing compared with polyolefins or polystyrene. Due to this fact, the additives such as plasticizers, stabilizers, slip agents etc. are used during manufacturing. As a result, the final compound becomes flexible and much more versatile. PVC can be used as a rigid compound or mixed with plasticizers to produce flexible grades.

PVC is differentiated according to K-value deduced from Fikentscher equation [9] into several groups. One of these types is non-plasticized PVC (UPVC) with properties whose combination is not generally available with other plastics. They are:

1. Low cost
2. Good resistance to burning (due to chlorine content)
3. Excellent weathering behaviour
4. Very good chemical resistance particularly to hydrocarbons
5. Rigidity and toughness
6. Low permeability of water vapour, oxygen and many organic volatile matters

[11]

The last item is closely connected to the topic of the present Master Thesis because permeability can be understood as the opposite property to barrier properties for plastics depend on the amount of plasticizer used in manufacture. UPVC is a good gas and vapour barrier, but these properties decrease with increasing plasticizer content, because of increased molecular chain mobility and intermolecular distances [12]. As a result, larger and more direct

pathways are created in the material for the diffusion of gases. Therefore, plasticized PVC (PPVC) was used as a matrix for creating PCN to enhancement barrier properties.

2.1.3 Applications of plasticized PVC

PPVC has a very wide utilization. It is caused by the low cost of compounds, their processing versatility, their toughness and durability, particularly in wire and cable insulation. Other important areas of application of PPVC sheet and films are for example seepage barriers, factory doors, baby pants, car trim, covering materials for book bindings and document cases and shower curtains. Moreover PPVC is used for the production of flooring and leatherette.

Thanks to excellent resistance to weathering in outdoor conditions, plastics membranes from PPVC are utilized as waterproofing road foundations and roof films in civil engineering.

The other application is production of tarpaulins. Their advantages are very good resistance against adverse weather conditions and spotting.

2.2 Clay minerals and clays

Common clays are naturally occurring minerals and thus are subjected to natural variability in their constitution. The purity of the clay can affect the final nanocomposite properties [13].

2.2.1 Definition of clay and clay minerals

The term **clay** is denoted to materials with a certain particle size range and physical properties. They can vary, depending upon the discipline that is operationally using the term. In geology, the term clay includes all particles smaller than 2 μm , in engineering it is sometimes reported as $<4 \mu\text{m}$. When the term "clay sized" particles is used, there are no connotations of composition. The term clay sized can comprise any material as long as it is within the particle size range is of less than 2 μm . Clay is often described as a fine grain material that is plastic if it is wet and is chiefly composed of hydrous alumino-silicate mineral [14].

Clay minerals can be defined in different ways. Some sources define them as part of general but important group within the phyllosilicates that contain large percentages of water trapped between the silicate sheets. Most of clay minerals are chemically and structurally analogous to other phyllosilicates but contain varying amounts of water and allow more substitution of their cations [15]. On the other hand, Weiss [16] defines clay minerals as groups containing all phyllosilicates and other minerals (such as minerals of allophane group, some hydroxide, oxy-hydroxide and oxides), that afford plasticity to clays and they can be cured after exsiccation or burning. These other minerals are only minority components of clays in contrast to phyllosilicates. According to Mineralogical society of America, clay minerals belong to the family of phyllosilicates and contain continuous two-dimensional tetrahedral sheets of composition T_2O_5 ($T = \text{Si, Al, Be, ...}$) with tetrahedra linked by sharing three corners of each, and with the fourth corner pointing in any direction. The tetrahedral sheets are linked in the unit structure to octahedral sheets, or to groups of coordinated cations, or individual cations [17].

2.2.2 Phylosilicates

Phylosilicates, or sheet silicates, are an important group of minerals where tetrahedron $[TO_4]$ and octahedron $[MA_6]$ (see Fig. 6) are of interest for building the phylosilicates. The central cations of tetrahedron are designated T, and beside the most frequent Si^{4+} they can include for example Al^{3+} , Fe^{3+} and Ge^{4+} . The central cations of octahedron are designated M, and they can include for example Al^{3+} , Fe^{3+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ca^{2+} and Li^+ . Symbol A is used here because there are some anions of octahedron, like O^{2-} , but also OH^{-1} or F^{-1} in phylosilicates [16].

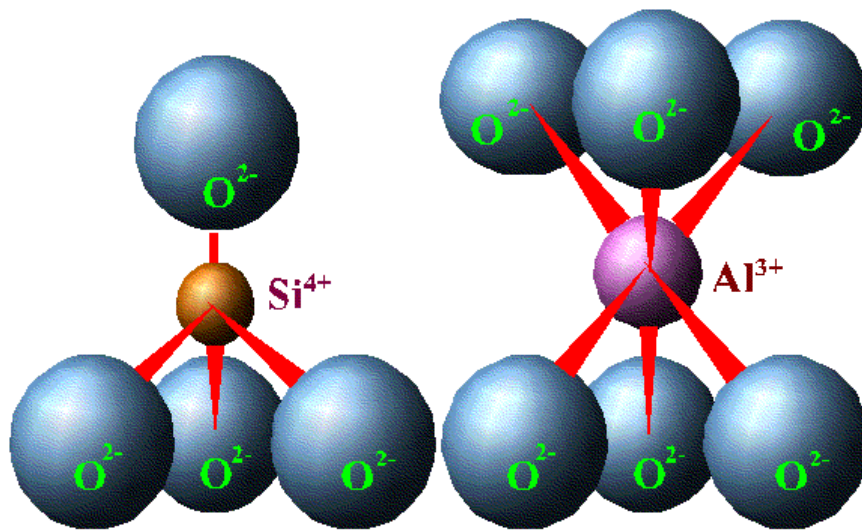


Fig. 6 Si-Tetrahedron and Al-Octahedron [18]

The basic structure of phylosilicates is based on interconnected six member rings of SiO_4^{-4} tetrahedra that extend outward in infinite sheets [19].

Tetrahedral sheets (Fig. 7) are composed of individual tetrahedrons and three of four oxygens are shared in each of them (in summary $\text{Si}_2\text{O}_5^{2-}$). They are arranged in a hexagonal pattern with the basal oxygens linked and the apical oxygens pointing up/down.

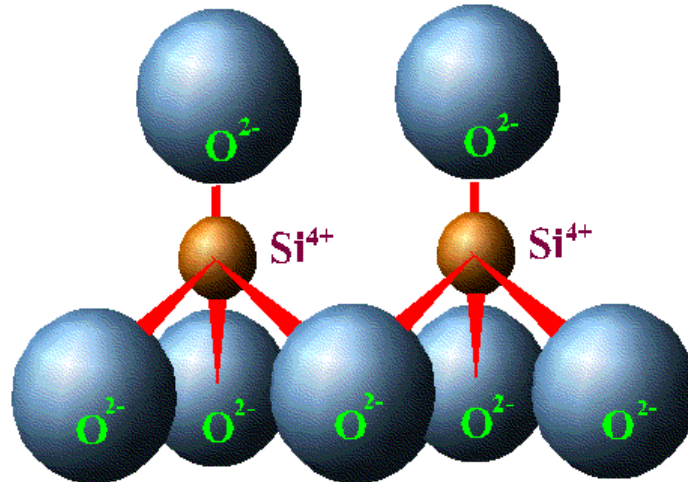


Fig. 7 The tetrahedral sheet [18]

Octahedral sheets (Fig. 8) are composed of individual octahedrons that share edges composed of oxygen and hydroxyl anion groups with Al^{3+} , Mg^{2+} , Fe^{3+} and Fe^{2+} typically serving as the coordinating cation. These octahedrons arranged in a hexagonal pattern are known as gibbsite sheet [5, 7, 15, 20 and 21].

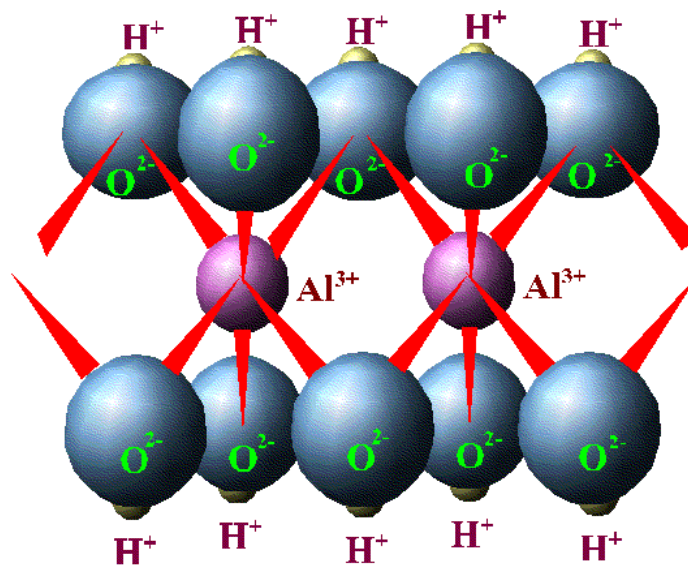


Fig. 8 The octahedral sheet [18]

Phylosilicates can be divided into two groups:

- 1) **Planar phylosilicates** - their structures include a continual two-dimensional periodic site of tetrahedron and octahedron.

Two types of structural unit produced by connection of tetrahedral and octahedral sites can be seen in the case of planar phylosilicates:

- layers 1:1 – when octahedral and tetrahedral sheet has one common plane of oxygenic atoms. These layers are constructed of one octahedral and one tetrahedral layer.
 - layers 2:1 – when octahedral and tetrahedral sheet has two common planes of oxygenic atoms. These layers are constructed of one octahedral and two tetrahedral layers with opposite polarity [16].
- 2) **Unplanar phylosilicates** - their structures contains periodic dislocation of planar phylosilicate structure. Moreover, in this case the planar structures can be bent or cylindrically rolled and can even have a spheroid character [16].

Clays can be classified into 7 groups [22]:

1. kaolinite group
2. montmorillonite/smectite group
3. illite (or clay-mica) group
4. chlorite group
5. sepiolite and palygorskite
6. mixed-layered clays
7. vermiculite

In the following we are going to deal with the group which is relevant to the present Master Thesis topic.

2.2.3 Smectite group

The term smectite is used to describe a family of expandible 2:1 phyllosilicate minerals with permanent layer charge between 0.2 and 0.6 charges per half unit cell. Smectites are constructed of a single octahedral sheet sandwiched between two tetrahedral sheets. The octahedral sheet shares the apical oxygens with the tetrahedral sheet and may be either dioctahedral or trioctahedral [23]. The structure of this group can be seen in Fig. 9.

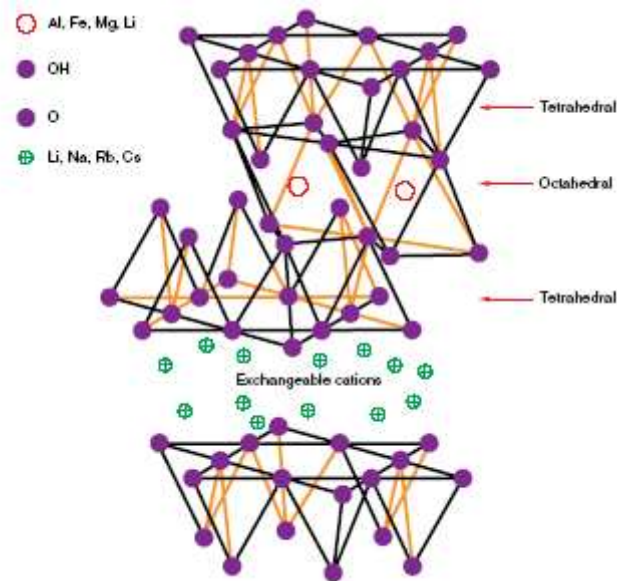


Fig. 9 The structure of 2:1 layered silicate [28]

Members of the smectite group include:

1. *Dioctahedral smectites*: montmorillonite, beidellite, nontronite and volkonskoit.
2. *Trioctahedral smectites*: hectorite, saponite, sauconite and stevensit.

The most important aspect of the smectite group is the ability of H₂O molecules to be absorbed between the sheets. It can cause the increase of mineral volume when mineral comes in contact with water. Thus, the smectites are expanding clays [19]. In other words, smectites swell in the presence of water, and also many organic liquids.

The interlayer (the space between the sheets) is hydrated and expandible; that is, the separation between individual smectite sheets varies depending on:

- 1) The type of interlayer cations (monovalent cations like Na⁺ cause more expansion than do divalent cations like Ca²⁺),

- 2) The concentration of ions in the surrounding solution,
- 3) The amount of water present in the soil.

The interlayer atoms are fairly loosely attached to the mineral surface, and therefore can be exchanged for other cations. For this reasons they are called **exchange cations**. For instance, if smectite clay with mainly Ca^{2+} ions comes in contact with sea water, they loose Ca^{2+} and accept Na^+ ions.

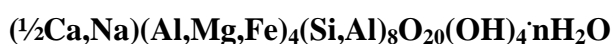
Cation exchange is a very important process in nature, and it partly regulates the natural water composition by absorbing and desorbing ions. The **cation exchange capacity** (CEC) is the measure of the charge imbalance of clay, and also the measure of the number of ions that can occupy the interlayer sites. The CEC varies according to the nature of the absorbed ions present in the interlayer sites. Kaolinite has very low CEC (3-15 meq/100g), whereas smectites may have large values (70-130 meq/100g) [24].

Soils with high concentrations of smectites can undergo as much as 30% volume change due to the wetting and drying. In other words, these soils have high shrink/swell potential [19]. Unlike the other clays, only smectite can absorb toxins. This property qualifies its structural uniqueness and differentiates them from all other clays. For this reason, smectite has become favourite clay for industrial and dietary usage [25].

2.2.4 Montmorillonite

The most common dioctahedral smectite is montmorillonite (MMT), discovered in 1847 in France (Montmorillon) by Damour and Salvétat. MMT is particularly attractive as reinforcement for the polymer–clay because it is environmentally friendly, readily available in large quantities with relatively low cost and its intercalation chemistry is well understood.

One of common formulas of montmorillonite is



however, the exact structure depends on the type of MMT.

The model structure consists of two fused silica tetrahedral sheets sandwiching an edge-shared octahedral sheet of either aluminium or magnesium hydroxide. The MMT layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 30 nm

to several microns. MMT has a very high aspect ratio (e.g. 10–1000, one gram of this clay has a surface area of 800 square meters [25]). Isomorphous substitutions of Si^{4+} for Al^{3+} in the tetrahedral lattice and of Al^{3+} for Mg^{2+} in the octahedral sheet cause an excess of negative charges within the montmorillonite layers. These negative charges are counterbalanced by cations such as Ca^{2+} and Na^+ situated between the layers. Due to the high hydrophilicity of the clay, water molecules are usually also present between the layers. Stacking of the layers leads to regular van der Waals gaps called interlayers or galleries.

The sum of the single layer thickness (0.96 nm) and the interlayer represents the repeat unit of the multilayer material, so called d-spacing or basal spacing, and is calculated from the (00l) harmonics obtained from X-ray diffraction patterns. The d-spacing between the silica-alumina-silica units for a Na-montmorillonite varies from 0.96 nm for the clay in the collapsed state to 200 nm when the clay is dispersed in water solution [3].

There are a number of descriptive terms for MMT, which are mainly based on geographic source, exchangeable cations, production process, and end use application.

3 PCN AND THE ENHANCEMENT OF BARRIER PROPERTIES

As mentioned above, polymer nanocomposites are prepared by dispersing a filler material into nanoparticles that form flat platelets. They have submicron dimensions, excepting their thickness, which is only about one nanometer. This dimensional disparity results in a large aspect ratio is a property conducive to barrier enhancement based on the principle of tortuous path migration [26, 27], in which impermeable nanolayers impede the diffusion of solvent molecules varied in intercalate or exfoliate structure. As Fig. 10 shows, the exfoliated nanocomposite restricts the diffusion path more in comparison with intercalated or conventionally filled micro composites [29]. In particular, a high length-to-width or aspect ratio of the clay lamellae is a key factor in maximizing tortuosity [30].

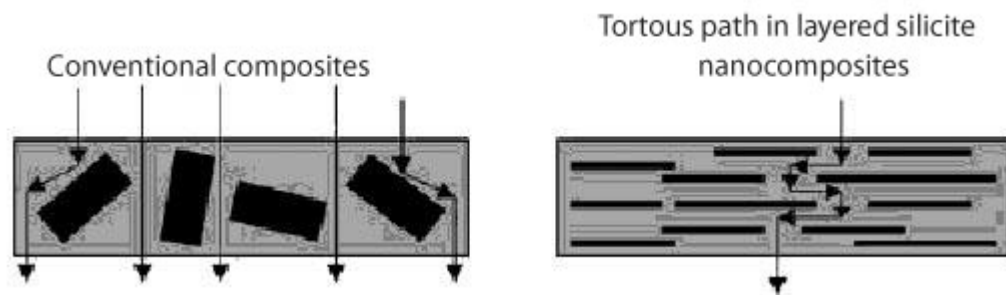


Fig. 10 The tortuous path migration [1]

Nanocomposites in general have improved properties even at low fillers content (<wt5%). Nanoclays create a “passive” barrier by impeding the diffusion of gases as they attempt to permeate through a plastic matrix [27]. The connection of the properties of polymer matrix and the clay nanofillers causes exciting enhancement namely of barrier and mechanical properties. Moreover, the size of particles assures very good clarity of PCN.

The barrier property of the polymer with nanoclay particles is reported for the various thermoset and thermoplastic materials. Osman et al. [31] determined the permeation coefficient decreasing asymptotically with increasing volume fraction of the organo-MMT inorganic part. Mohan et al. [29] confirmed considerably decreasing the mass uptake using epoxy/clay nanocomposites to the pure matrix. Their research demonstrated that the addition of organo-MMT served as good weight loss arrester in all the mediums than unmodified clay system. Due to presence of organoclay, the torturous path of the solvent medium increases, the diffusion path hinders and also mass uptake decreases in the polymer matrix.

4 TESTS OF BARRIER PROPERTIES AND DATA ANALYSIS

Barrier properties in polymers are necessarily associated with their inherent ability to permit exchange, to higher or lower extent, of low molecular weight substances through mass transport process such as permeation. Permeation is generally envisaged as a combination of two processes i.e. solution and diffusion. A permeate gas is first dissolved into the upstream face of the polymer film, and then undergoes molecular diffusion to the downstream face of the film where it evaporates into the external phase again. A solution-diffusion mechanism is thus applied, which can be formally expressed in terms of permeability P , solubility S and diffusion D coefficients by

$$P = D \cdot S \quad (1)$$

The solubility coefficient S is thermodynamic in nature, and is defined as the ratio of the equilibrium concentration of the dissolved penetrant in the polymer to its partial pressure p in the gas phase (Henry's law). In polymers, this law is usually obeyed at low penetrant concentrations, i.e. when S is independent of concentration (or of the partial pressure). The diffusion coefficient D characterises the average ability of the sorbed permeate to move through the polymer chain segments, and is determined from Fick's first law of diffusion, i.e. the flux of the permeant J is proportional to the local gradient of concentration c through the thickness of the polymer film l [32].

Equation 1 has also been often considered to describe the gas transport properties of composites composed of impermeable fillers dispersed in a polymer matrix [33].

Other theoretical approaches for predicting barrier properties of polymer/clay nanocomposites based on non-Fickian behaviour (anisotropic) have been discussed in literature [33-38]. However, the nanocomposite morphology must be the one described in Fig. 10 (only rarely achieved) and the filler particles must not interact with the diffusing molecules. For this reason, in this work we think about Fickian behavior.

4.1 Water vapour transmission

This method belongs to barrier properties and is used for the detection of the permeability of water vapour through materials. This characteristic is decisive especially for packaging materials and films used in civil engineering.

Very often material is characterized by water vapour permeability, which is defined as the rate of water vapour transmission through the unit area of a flat material of unit thickness induced by unit vapour pressure difference between two specific surfaces, under specified temperature and humidity conditions.

The permeability of a nanocomposite system normally depends on the clay content, length-to-width ratio, relative orientation and degree of dispersion (intercalated, exfoliated, or intermediate state) of the silicate layers [30].

Permeability is calculated according to this equation:

$$P = \frac{WVT}{\Delta p} \cdot h = \frac{G}{t \cdot A \cdot S \cdot (R_1 - R_2)} \cdot h \quad (2)$$

Where P ... permeability [g/Pa.s.m]

Δp ... vapour pressure difference [Pa]

h ... thickness of sample [m]

G/t ... slope of the straight line [g/h]

S ... saturation vapour pressure at test temperature [mm Hg]

R_1, R_2 ... relative humidity at the source (50%) and at the vapour sink (either 0% for Desiccant method or 100% for the Water method)

A ... test area [m²]

t ... time [h]

WVT ... water vapour transmission rate [g/h.m²]

WVT is defined as the steady water vapour flow in unit time through unit area of a body, normal to specific parallel surfaces, under specific conditions of temperature and humidity at each surface.

WVT is calculated as:

$$WVT = G/t \cdot A = (G/t)/A \quad (3)$$

Where G ... weight change [g]

G/t ... slope of the straight line [g/h]

Measuring of water vapour transmission can be provided by two basic methods, both the Desiccant method and the Water method. These methods can be varied by service condition either with one side wetted or with low humidity on one side and high humidity on the other. Agreement should not be expected between results obtained by different methods.

Kim et al. [34] was used this method to determine moisture permeation of organoclay-epoxy nanocomposites.

4.2 Solvent permeation resistance

The important properties by this method are the change of weigh and volume. The first step of swelling may be usually accompanied by rapid polymer saturation, and then slow changes with linear behaviour could follow.

The change of weight is calculated according to the equation:

$$B_m = \frac{m_1 - m_0}{m_0} \cdot 100 \quad (4)$$

Where B_m ... the change of weight [%]

m_0 ... the weight of samples before measurement [g]

m_1 ... the weight of samples after time t [g]

FTIR can offer the efficient way to appraise changes during polymer saturation.

4.3 Determination of water absorption

To determine the improvement in barrier properties of a nanocomposite compared to neat polymer, one may carry out water absorption tests. Here one immerses a sample in water and measures the amount of water absorbed in a fixed amount of time; barrier properties are considered to have been improved if the amount of moisture absorbed decreases with added nanofiller like in Rana's paper [35]. This method can be expressed by two methods:

4.3.1 Percentage by mass of water absorbed

This appropriate formula can be used to calculate the percentage change in mass relative to the initial mass:

$$c = \frac{m_2 - m_1}{m_1} \cdot 100 \quad (5)$$

or

$$c = \frac{m_2 - m_3}{m_1} \cdot 100 \quad (6)$$

Where c ... water content [%]

m_1 ... mass of the test specimen after initial drying and before immersion [mg]

m_2 ... mass of the test specimen after immersion [mg]

m_3 ... mass of the test specimen after initial drying and final drying [mg]

4.3.2 Determination of the water content at saturation and the diffusion coefficient using Fick's law

To compute the diffusion coefficient from data on mass gain as a function of time, one may use Fickian theory. For unfilled samples, the process of one-dimensional, unsteady diffusion is governed by [34, 35]

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (7)$$

in which c is the concentration of the diffusion species, t is time, x is the position in the diffusing direction, and D is the diffusion coefficient or diffusivity.

Upon solving eq. 7 with constant boundary conditions, the relative moisture uptake is expressed as

$$\frac{M_t}{M_\infty} = \left[1 - \sum_0^\infty \frac{8}{(2n+1)^2 \pi^2} \exp\left[\frac{-D(2n+1)^2 \pi^2 t}{h^2} \right] \right] \quad (8)$$

Where M_t ... mass gain at reduced time

M_∞ ... maximum mass gain at the equilibrium state

h ... the sample thickness

At the initial stages of diffusion, the solution Fick's law at small times reduces to

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi h^2} \right)^{1/2} \quad (9)$$

In our case it could be expressed by

$$1 - \frac{c}{c_s} = \frac{8}{\pi} \exp\left(-\pi^2 \frac{D \cdot t}{l^2}\right) \quad (10)$$

Where c_s ... water content at saturation [%]

t ... time of immersion of the test specimen in water or humid air [s]

l ... samples thickness [m]

Diffusion coefficient is computed from initial slope $\ln\left(1 - \frac{c}{c_s}\right)$ vs. t using short-time water-uptake data.

4.4 Exposure to liquid chemicals

It is based on exposition of foil samples for roof hydro-insulation by chemical liquids. This test possibly represents the effect of chemicals on the hydro-insulation foils.

Mass change could be evaluated:

$$m_2 - m_1 \text{ (wet way)} \quad \text{or} \quad m_3 - m_1 \text{ (dry way)} \quad (6)$$

Percentage weight change can be described by similar equation as in chapter 4.3.1 and for the determination of areal weight change can be used this relation:

$$(m_2 - m_1) / A \text{ (wet way)} \quad \text{or} \quad (m_3 - m_1) / A \text{ (dry way)} \quad (7)$$

Where m_1, m_2, m_3 ... similar meaning as in chapter 4.3.1.

A ... initial surface area of samples [cm^2]

5 OBJECTS

- Investigation of barrier properties using Water vapour transmission, Solvent permeation resistance, Determination of water absorption and Exposure to liquid chemicals

- Evaluation and results discussion

- Summarizing the effect of clay on the barrier properties of PCN

II. PRACTICAL PART

6 MATERIALS AND METHODS

6.1 Used materials

6.1.1 Polyvinyl chloride compound

In the first stage of this work, suspension type of PVC K65 – Neralit 652 from Spolana Neratovice (Czech Republic), stabiliser Lankromark LZB 968 produced by Akros Chemicals (United Kingdom), plasticizer dioctylphthalate from Deza Valašské Meziříčí (Czech Republic) and co-stabiliser (epoxidised soy bean oil) – Drapex 39 from Crompton Vinyl Aditives (Germany) were used for preparation of PVC compound. Composition of the compound, which was supplied by Fatra Napajedla, can be seen in the Table 1.

Table 1 Composition of the PVC compound used for foil production

PVC K65 - Neralit 652	735 g
Lankromark LZB 968	13 g
DOP	242 g
Drapex 39	10 g
Total	1000g

NERALIT 652 is poly (vinyl chloride) of medium molecular weight. It has porous structure of grain and it is suitable for processing to plasticized products. Furthermore, it is a polymer of high chemical purity with good thermal stability and it can be used to make transparent products. It absorbs plasticizers well and can be processed by dry blend technology. It presents good flow properties. It is designed for processing to plasticized products by calendaring (assembling films, packaging films, semi-finished products for production of toys), which is useful for preparation of our samples.

LANKROMARK LZB 968 belongs to the category of liquid barium/zinc self-lubricating stabilisers. Lankromark LZB 968 is suitable for applications where great length of stability and outstanding colour hold are required. These stabilisers are widely used in the processing of plasticised PVC by calendaring. They proved successful replacements for cadmium containing stabilisers in all plasticised PVC applications.

DIOCTYLPHTHALATE (DOP) in other words di-2-ethylhexylphthalate, is colourless sometimes delicately yellowish medium viscosity liquid with a characteristic odour. It is often used as plasticizer into plastic materials (in this case PVC).

DRAPEX 39 (i.e. epoxidised soy bean oil) is a non-toxic co-stabiliser used in rigid and plasticized PVC and other chlorine containing polymers. Its stabilising action is based on ability to bind hydrogen chloride. Additionally, as a co-stabiliser for organic or metal soap stabilisers it has a positive effect on the long-term heat stability.

6.1.2 Nanofillers

Montmorillonite from Southern Clay Products (USA), namely Cloisite® Na⁺ and Cloisite® 30B, were used as a source of nanoparticles. Cloisite® 30B is a montmorillonite modified with a quaternary ammonium salt; Cloisite® Na⁺ is a natural montmorillonite.

Both fillers are used as additives for plastics to improve barrier properties. Some typical properties can be seen in Table 2.

Table 2 Some typical properties of Cloisite® 30B and Cloisite® Na⁺

Treatment/ Properties	Organic Modifier	Modifier Concentration	% Moisture
Cloisite® Na ⁺	None	None	4 - 9 %
Cloisite® 30B	MT2EtOH ²	90 meq ³ /100g clay	< 2 %

6.1.3 Intercalation and co-intercalation agents

Diethyleneglycol and polyethyleneglycol from Aldrich-Lachema (Czech Republic) were used as intercalation agents for modification of MMT. In addition, tricresylphosphate produced by Sigma-Aldrich (Czech Republic), DOP from Deza Valašské Meziříčí (Czech Republic) and isodecyl diphenyl phosphate produced under commercial brand Santicizer® 148 from Ferro Corporation (Belgium) were chosen as co-intercalation agents.

²MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride

³ The equivalent (eq) is formally defined as a mass in grams of a substance which react with 6.022×10^{23} electrons

DIETHYLENEGLYCOL (DEG) molecular structure is HO-CH₂-CH₂-O-CH₂-CH₂-OH. It is a clear, hygroscopic, odorless liquid. It is miscible with water, other alcohols, diethyl ether and acetone, but insoluble in benzene and carbon tetrachloride.

POLYETHYLENEGLYCOL (PEG) is commercially important polyether. It is a polymer of ethylene oxide with shorter chain length despite polyethylene oxide with similar monomer unit. It is coupled to hydrophobic molecules to produce non-ionic surfactants.

TRICRESYLPHOSPHATE (TCP) in other words tritoluylphosphate, is generally used as antiwear additives.

ISODECYL DIPHENYL PHOSPHATE (IDP) combines the advantages of flexibility at low temperatures, the effectiveness and the ease of use of DOP, with the fireproofing properties of phosphates. As a result, it can be substituted part-by-part for DOP with increasing fire resistance of the final product.

6.1.4 Hydro-insulation membranes

Due to comparison of barrier properties our samples with products on the market, hydro-insulation membranes for insulation of roofs and sub-grade construction from Fatra Napa-jedla (Czech Republic) were selected.

FATRAFOL 803 is a non-reinforcement hydro-insulation membrane of PPVC produced by membraneing and lamination processes. Due to its outstanding chemical resistance it is designed mostly as an insulation of overground and underground parts of constructions against seepage water as well as in applications as a waterproof membrane in insulation systems against penetration of leachates into ground water. Fatrafol 803 is also suitable for insulating tunnels, hydraulic constructions, underground reservoirs, containment pits, agricultural structures and industrial products storage sites. For our measurement was chosen brown membrane 1.5 mm thick.

FATRAFOL 804 membrane is designed mostly as an accessory to FATRAFOL roof membranes to be used in complicated roof surfaces and for tailoring of details. Grey membrane 2.0 mm thick was used as comparative material.

STAFOL 914 is a homogeneous hydro-insulation membrane of PPVC, manufactured by calendaring. STAFOL 914 is devised for insulating constructions against subsoil moisture. It is especially suitable for insulation of floors in industrial, commercial and storage halls. The membrane can be also used as a waterproof layer on masonry against rising moisture

both in newly built structures and in old buildings as a watertight insulation, as a water-proofing in environment with high aggressivity (places with inorganic acids, bases and their salts), as a protective or separation layer in floor structures, etc. In this case black membrane 0.8 mm thick was utilized to properties comparison.

6.1.5 Medical material

Due to utilization PPVC in the health care, measurement of barrier properties were employed on medical materials such as blood can and urological bag. Material to production urological bags namely Foil 902 was acquired from Fatra Napajedla (Czech Republic). Testing blood can comes from Transfusional department of Tomas Bata hospital in Zlin.

6.2 Composition of samples

6.2.1 PVC/clay nanocomposites

As table 3 shows, the organically modified montmorillonite was used as filler in PVC suspension-type compound; commercially modified montmorillonite Cloisite® 30B was also used in order to compare the properties with natural montmorillonite Cloisite® Na⁺ and non-filled PVC.

Table 3 Composition of PVC/clay nanocomposites

Indication of sample	Nanofiller	Nanofiller concentration	Intercalation agent	Co-intercalation agent	ratio filler:intercalat:co-intercalate	
PVC/Na5/DEG0.5	Cloisite Na ⁺	5wt%	DEG	-	1 : 0.5	
PVC/Na3/DEG0.5	Cloisite Na ⁺	3wt%		-	1 : 0.5	
PVC/Na5/DEG1	Cloisite Na ⁺	5wt%		-	1 : 1	
PVC/Na3/DEG1	Cloisite Na ⁺	3wt%		-	1 : 1	
PVC/Na5/DEG/DCP	Cloisite Na ⁺	5wt%		DCP		1 : 0.25 : 0.25
PVC/Na3/DEG/DCP	Cloisite Na ⁺	3wt%				1 : 0.25 : 0.25
PVC/Na5/DEG0,5/TCP	Cloisite Na ⁺	5wt%				1 : 0.5 : 0.5
PVC/Na3/DEG0,5/TCP	Cloisite Na ⁺	3wt%				1 : 0.5 : 0.5
PVC/Na5/DEG/TCP	Cloisite Na ⁺	5wt%		TCP		1 : 0.25 : 0.25
PVC/Na3/DEG/TCP	Cloisite Na ⁺	3wt%				1 : 0.25 : 0.25
PVC/Na5/DEG/IDP	Cloisite Na ⁺	5wt%		IDP		1 : 0.25 : 0.25
PVC/Na3/DEG/IDP	Cloisite Na ⁺	3wt%				1 : 0.25 : 0.25
PVC/30B5/IDP	Cloisite 30B	5wt%		commercially intercalated		1 : 0.25
PVC/30B5/TCP	Cloisite 30B	5wt%			TCP	
PVC/30B3/TCP	Cloisite 30B	3wt%				1 : 0.25
PVC/Na5/PEG	Cloisite Na ⁺	5wt%	PEG	-	1 : 0.5	
PVC/Na5/PEG/DOP	Cloisite Na ⁺	5wt%		DCP	1 : 0.25 : 0.25	
PVC/Na5/PEG/TCP	Cloisite Na ⁺	5wt%		TCP	1 : 0.25 : 0.25	
PVC/Na5/PEG/IDP	Cloisite Na ⁺	5wt%		IDP	1 : 0.25 : 0.25	
PVC/Na5	Cloisite Na ⁺	5wt%	-	-	-	
PVC/30B5	Cloisite 30B	5wt%	commercially intercalated	-	-	
PVC/IDP	-	-	-	IDP	-	
PVC/TCP	-	-	-	TCP	-	
PVC	-	-	-	-	-	

6.2.2 Commercial membranes

The compositions of hydro-insulation membranes and medical materials are not known. But these raw materials usually are created by mixture (in weight parts):

- ✦ Suspension type of PVC – 55 to 70

- ✦ Plasticizers (mostly phthalates) – 25 to 30
- ✦ Fillers, pigments – 0 to 10
- ✦ Others (stabilisers, lubricants, modifiers) – 1 to 3

6.3 Sample preparation

Preparation of PCN can be divided into four operations:

1. PVC compound was prepared in the fluid mixer PAPANMAIER. First, the powder components were filled into the cold mixer. After that, blending and input of heating steam into double covering of the mixer were switched on. All this process was run at the mixing velocity 600 rpm. Then the mixture was heated to the temperature of 40-45°C, when the liquid components were added. At 60 °C the input of heating was switched off and cooling by water started. Finally, the mixture was cooled to less than 40°C.

2. Organic modification of MMT was run in several steps:

- Intercalation of MMT Na⁺

Several samples of organo-montmorillonite were prepared by modification of sodium montmorillonite using DEG and PEG as main intercalation agents by ion-dipole interaction.

- Intercalation of Cloisite® 30B

Cloisite® 30B is commercially modified with a quaternary ammonium salt by ion-exchange interaction.

- Co-intercalation

TCP, DOP and IDP (Santicizer - commercial brand) were added during the intercalation process. Co-intercalation agents were intercalated by ion-dipole interaction.

First of all the Cloisite® Na⁺ was heated at 80°C under slow stirring for ten minutes to evaporate the moisture. Then the alcohol used as intercalation agent (DEG or PEG) was added gradually to the clay. After this, a plasticizer or additive (DOP, TCP, Santicizer) was introduced to the sample. During addition the temperature was maintained at 80°C. Consequently, the sample was held at the temperature of 80°C for 10 minutes under in-

tensive comixture. Finally, the temperature was increased to 90°C and the sample was intensively mixed for another 10 minutes. The process of preparation of the samples with Cloisite® 30B was the same but no alcohol was used.

The ratio of individual components in the intercalated samples can be seen in Table 3.

3. Organically modified nanofillers were mixed with polymer matrix in the molten state. Firstly, PVC mixture and intercalated MMT were dry-mixed by shaking in a bag. For good dispersion of intercalated MMT into PVC matrix, Buss KO-kneader (L/D = 30), a single screw machine was selected. The process was run at the temperatures in 4 zones from 130°C till 150°C at 67 rpm. The temperature at the extrusion head was 150°C. The extruded string was immediately granulated.

Acquired granules were used for film preparation by calendering on a laboratory open mill with dimensions 300x600 mm (the temperature of the front mill was 159°C and the rear mill 158°C). The obtained films were 0.1 and 0.5 mm thick.

The samples for measuring WVT were cut off the prepared 0.1 mm thick films and commercial membranes in the shape of a circle with a 48 mm diameter. Nine samples of every mixture (three samples for Desiccant method and six for Water method) were prepared and then the thickness of each was measured three times.

Further, test specimens for solvent permeation resistance were cut from square-shaped plates (125 x 125 x 2 mm) prepared by moulding 2 min at 160°C of foil 0.1 mm thick. Required dimension of test specimens were 10 x 50 mm with 2 mm thickness. For each material evaluated, the use of three test specimens was necessary.

Samples for testing determination of water and exposure to liquid chemicals fulfilled the relation for reinforced plastics affected by anisotropic diffusion effect. That means that 50x50 mm square test specimens were cut from 0.5 mm thick foil. In spite of this, square-shaped samples from commercial membranes satisfied requirements for finished products or sheets, for this reason samples with length and width 60 mm were cut. For each material and method, tests at least three specimens were required.

6.4 Methods of barrier properties

6.4.1 Standard method for vapour water transmission of materials

The WVT was measured according to standard ASMT E96, using both Water and Desiccant method. The apparatus for these methods can be seen in the Fig. 8. The test dish and ring were from aluminium. The empty apparatus and the specimen were weighted (with accuracy 0.0001 g). Then either 10 g of distilled water was put into the dish or 20 g of anhydrous CaCl_2 in the form of small lumps with size between 0.6 to 2 mm. After it, the individual parts of apparatus were put together (as in Fig. 8) by closing with the aluminium ring. The system was weighted again and finally the apparatus was put into the environment with aluminium ring either downwards by Water method or upwards by Desiccant method.

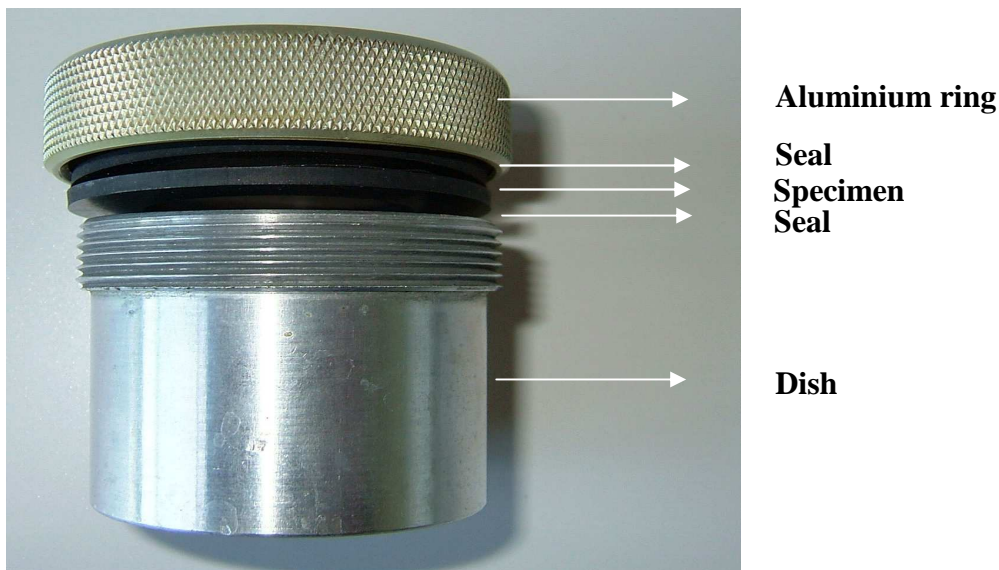


Fig. 8 The apparatus for measuring WVT

The test was run under temperature 37°C and relative humidity 50%. The essence of this method was measuring change in mass (it depended on using method) in a specific time intervals during 1 month. Periodic weightings determine the rate of water vapour movement through the specimen either into the desiccant or from the water to the controlled atmosphere.

6.4.2 Solvent permeation resistance

This method consisted of immersion each sample into the solvent, namely octane, in the test tube without touching side of test tube and being whole immersed. Then the samples were weighted (with accuracy 0.0001 g). Furthermore, they were put into the test tube with solvent and were plugged.

The essence of this method was measuring the weigh change in a specific time intervals during 37 days. The test was run by room conditions.

The structural changes were characterized by infrared spectroscopy. The spectra were obtained on a FTIR spectrometer Nicolet Avatar 320 in ATR technique mode. For each sample 64 scans were recorded in the spectral range $4000 \times 650 \text{ cm}^{-1}$.

6.4.3 Determination of water absorption

The test was performed according to standard ČSN EN ISO 62. Test specimens are immersed in distilled water a 23°C or in boiling distilled water, or exposed to 50% relative humidity, at a given temperature for 8 days.

Before measuring, all replicate test specimens were dried in an oven maintained at 50°C for 24 h. Samples were put to bakers containing solution closed at the top with polyethylene foil to prevent evaporation. The amount of absorbed water by the test specimen was determined by periodically measuring its mass change, i.e. the difference of its initial mass from that after exposure to water, and was expressed as a percentage of the initial mass. If required, the amount of water lost after drying the test specimens can also be determined.

6.4.4 Exposure to liquid chemicals

This technique was measured by fitting two standards together, namely ČSN EN 1847 and ČSN EN ISO 62. This test was conducted by immersing the various samples in 0.1 M salt solution at a room condition.

All measurement steps were similar as in paragraph 6.4.3.

7 RESULTS AND DISCUSSION

7.1 Standard method for water vapour transmission of materials

Standard method for vapour water transmission was selected as the first step for characterization barrier properties of materials. At first, samples (see Table 3 and commercial membranes) were measured using Water method (see paragraph 4.1). The result of the rate of water vapour transmission (WVTR) may be determined either graphically or numerically.

Periodic weight-decrease data for aluminium dish assembly used for water vapour transmission rate and permeability are shown in Fig. 11. Weight decrease depending on time was plotted. The slope of curve tends to straighten (Fig. 12 – green area) inscribed water vapour transmission rate. It is obvious, in each case; a steady state is attained after nearly 200 h.

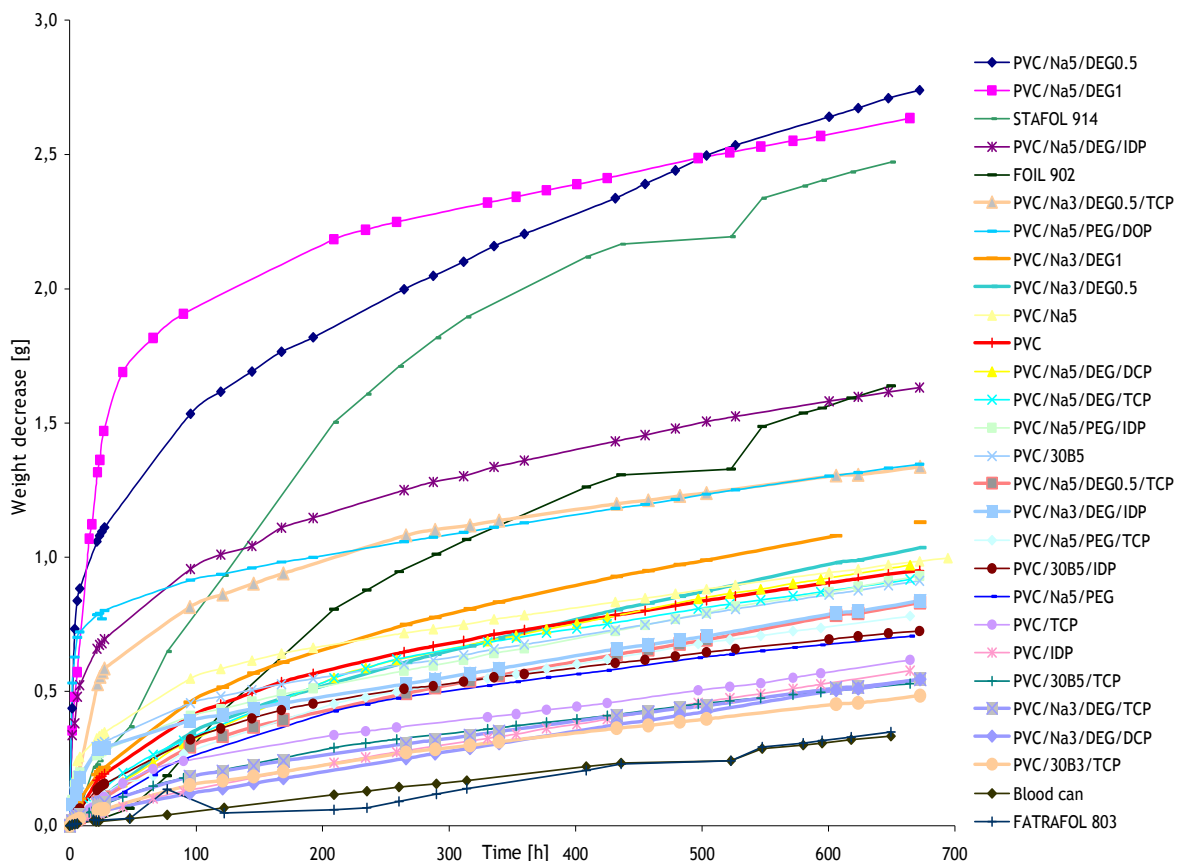


Fig. 11 Weight decrease as a function of time

Samples with smaller weight decrease than rigid PVC are shown in Fig 12. As can be seen, in most cases, samples containing TCP as co-intercalation agent belong among samples with low weight changes. Additionally, commercial membranes FATRAFOL 803 and Blood can demonstrate the lowest weight change of all. However, FATRAFOL 803 data could not be reproduced due to higher sample thickness than the rest samples.

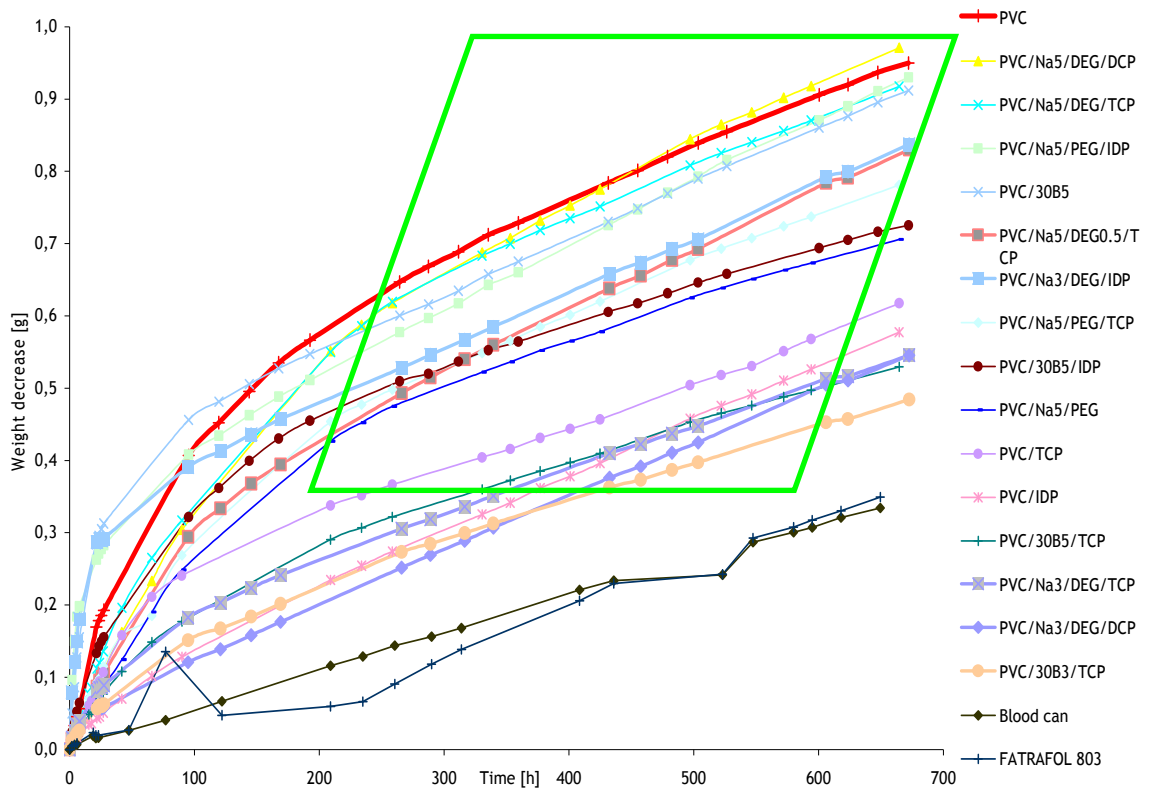


Fig. 12 Weight decrease on time dependence – materials with smaller weight decrease than unfilled PVC compound

Measured data were also numerically analysed. For this reason regression-analysis of the weight decrease as a function of time according to equation 3 gives the water vapour transmission rate.

The calculated WVTR is compared to unfilled PVC compound in Fig. 13. The obtained mathematical WVTR data (see Table 7 in Appendix) were affirmed graphical statements.

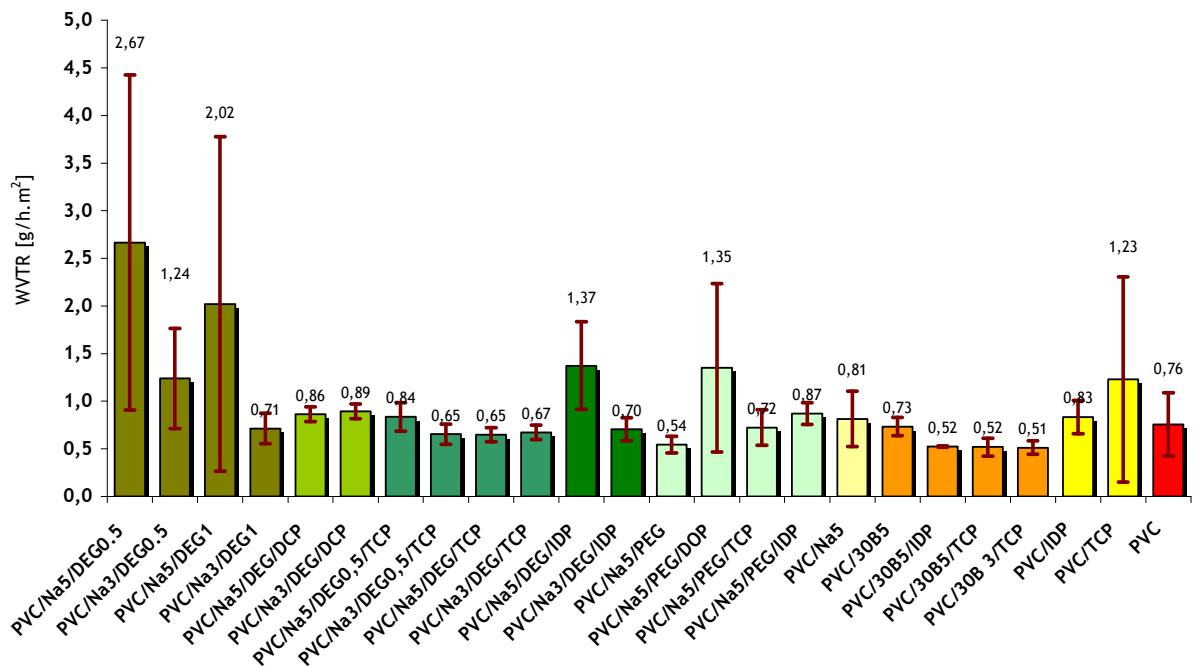


Fig. 13 Graphic comparison of calculated water vapour transmission rate comparison of samples

Commercial membranes were also analysed, but for better view they are further compared in percentages.

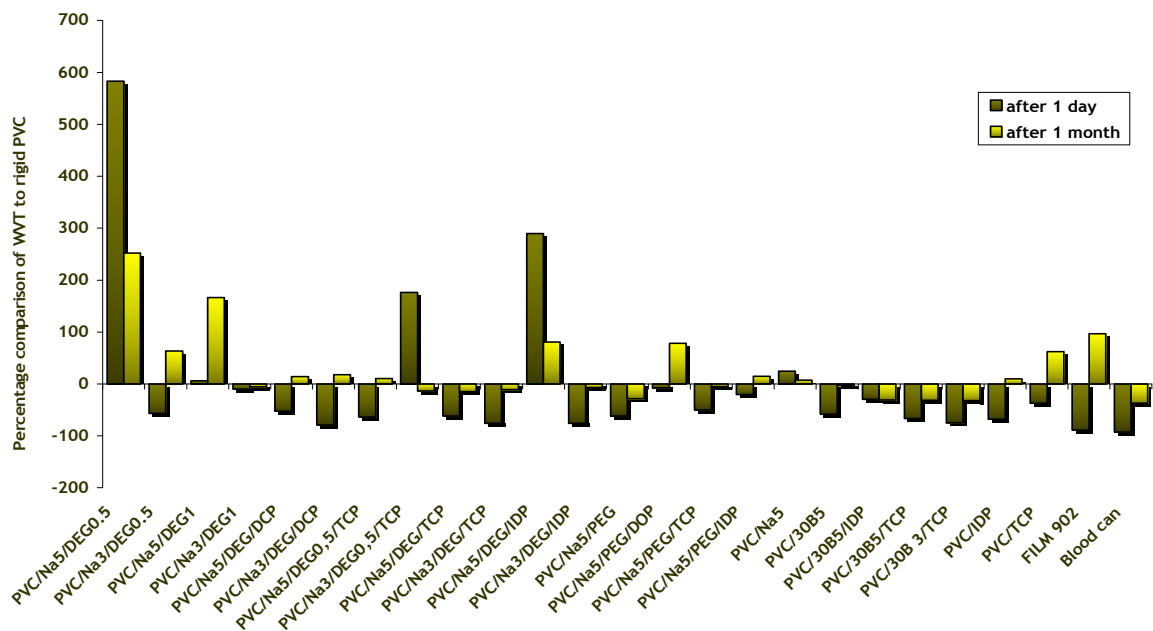


Fig. 14 Percentage comparison of mathematical WVTR to unfilled PVC compound both after 1 day and 1 month measuring

If the material values are less than that of unfilled PVC compound (that means negative values in Fig. 14), it refers to enhancement of barrier properties. On the other hand, the properties downgrade of some nanocomposite samples could be probably caused by poor particles bonding to the matrix or degree of exfoliation.

Afterward, moisture permeability was calculating according to equation 2. Data are shown in Fig. 15 and also in Table 7 in Appendix.

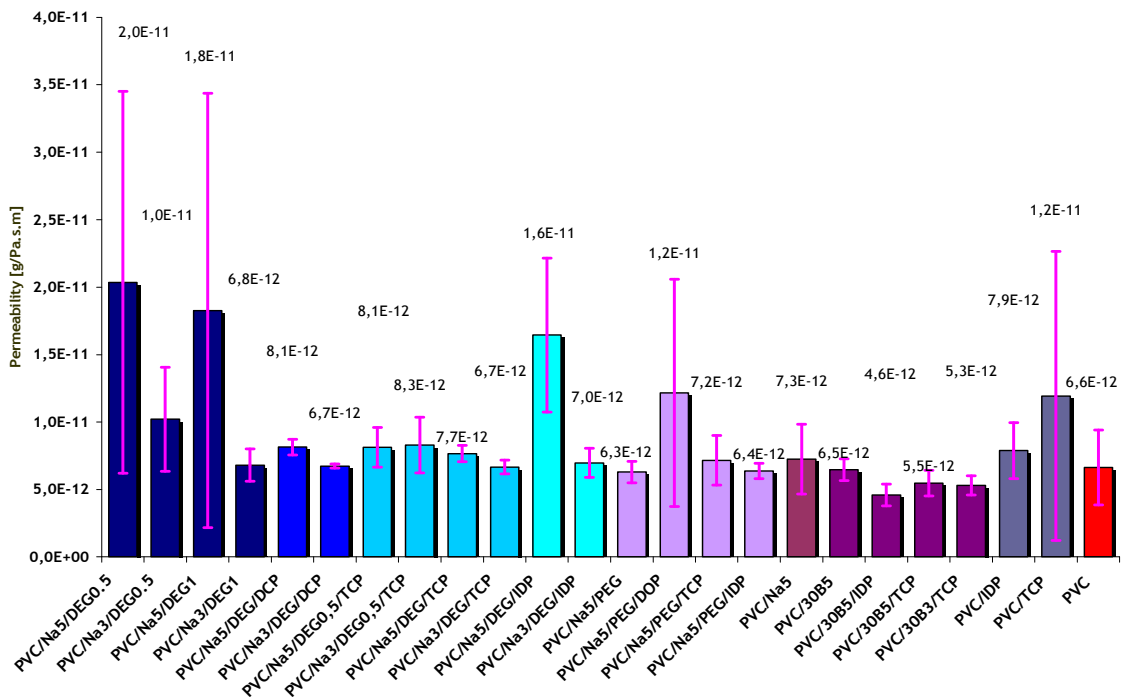


Fig. 15 Graphic permeability comparison of samples

In spite of expectation, every nanocomposite samples have not better permeability than rigid PVC. However, it is obvious, that samples with Cloisite ® 30B show low values than the others. It should be attributed to different degree of exfoliation and dispersion of clay particles.

As previous, permeability values of samples were percentage compared with those of commercial membranes to unfilled PVC compound (Fig. 16).

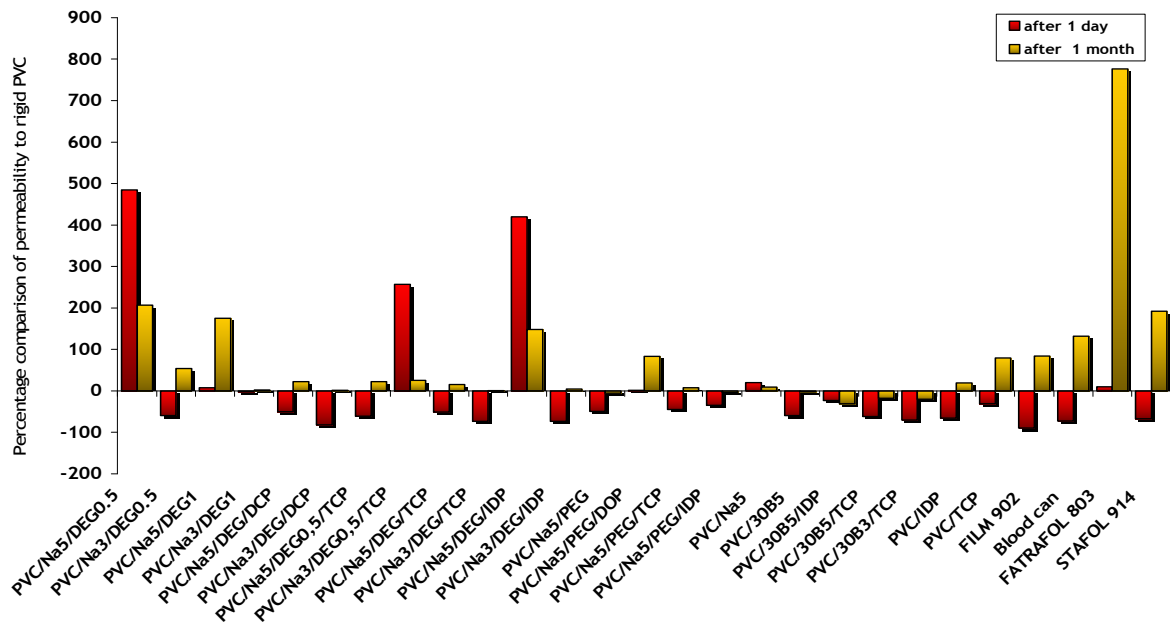


Fig. 16 Percentage comparison of moisture permeability of tested samples to unfilled PVC compound both after 1 day and 1 month measuring

As can be seen in Fig. 14 and 16, WVTR and permeability should be evaluated also after 24 hours (this data are expressed in Table 6 in Appendix). However, these calculated data are not exact due to absent of linear area for evaluation.

For further barrier testing method were selected only samples with similar or lower permeability value than rigid PVC. Nanocomposite samples, namely PVC/Na3/DEG1, PVC/30B5/IDP, PVC/Na5/PEG, PVC/Na3/DEG/DCP, PVC/30B5/TCP, PVC/Na5/PEG/IDP, PVC/Na3/DEG/TCP, PVC/30B3/TCP, PVC/Na5, PVC/30B5 were further measured and compared with unfilled PVC compound and commercial membranes.

This samples were represented widely area of point of view of each components effect on barrier properties. We could describe for example effect of filler content on these properties.

Moisture permeation, in other words ability of a material to resist moisture to penetrate through its thickness, was also measured using Desiccant method. Fig. 17 presents the weight gains measured from permeability test, which is made up of moisture absorbed by the desiccant in the dish as well as that present in the sample.

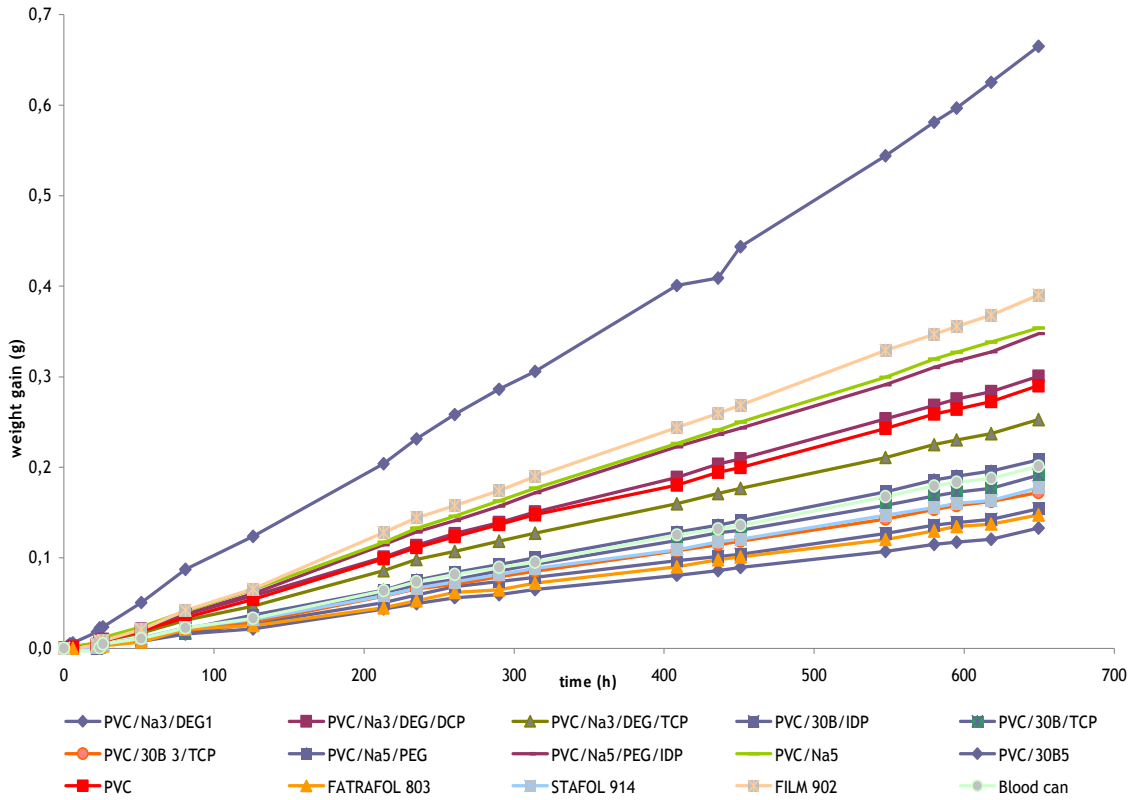


Fig. 17 Weight-gain as a function of time

In spite of Water method, weight gains have linearly growing trend already from starting point. It was confirmed that agreement should not be expected between results of these two methods.

The improved nanocomposite barrier behaviour is illustrated by these examples (Fig. 18 and 19).

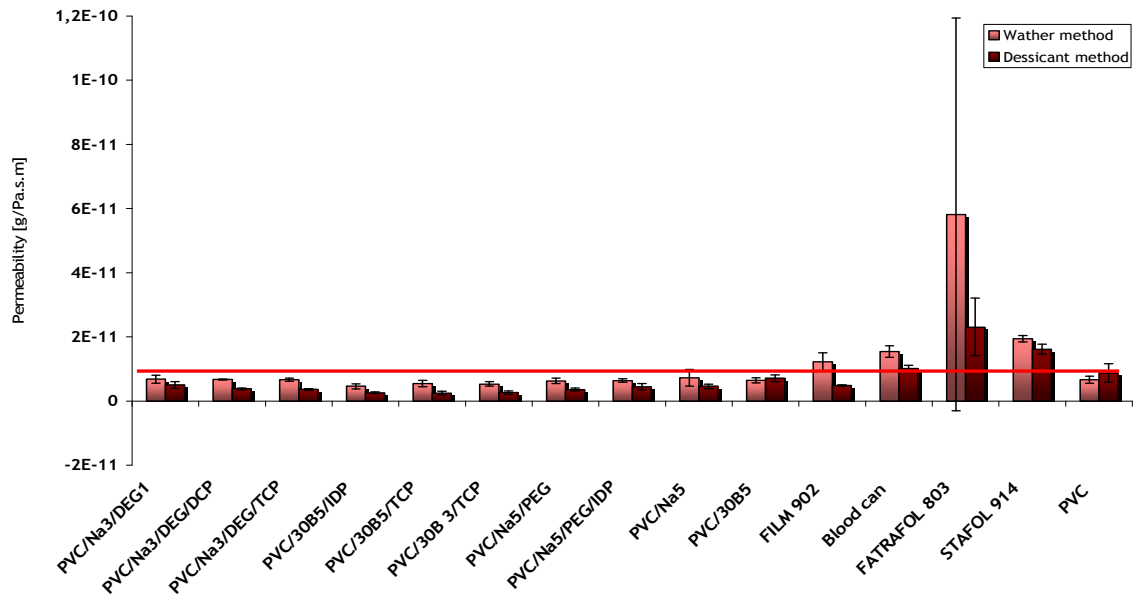


Fig. 18 Comparison of permeability measured using Water and Desiccant methods

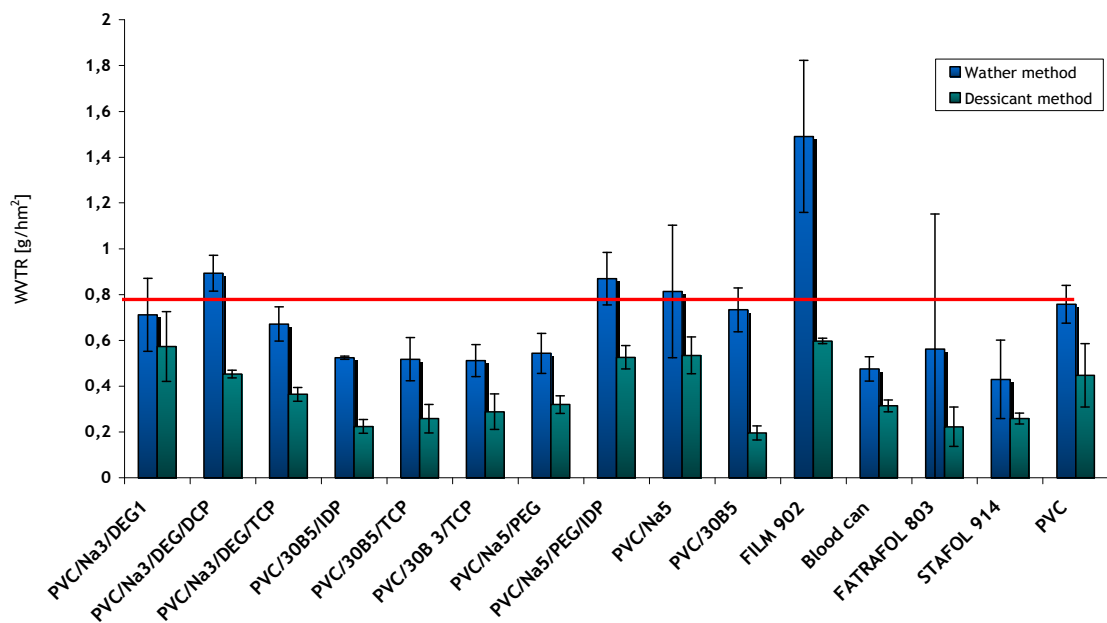


Fig. 19 Comparison of WVTR measured by Water and Desiccant methods

From achieved results (see Tables 7 and 9 in Appendix) it is obvious, that the addition of co-intercalated Cloisite® 30B reduce the permeability by in average 23% using Water method and 70% using Desiccant Method to unfilled PVC compound after 1 month of measuring. In comparing, samples contenting only Cloisite® 30B performed 3% enhancement by Water method and 18% by Desiccant method. It noted that addition of co-intercalation agents into PCN system is achieved higher barrier resistance.

Further, it could be deduced result from permeability values showed in Table 7 in Appendix. Only 3%wt. nanofiller contain leads to dramatically enhancement of p than 5%wt. nanofiller contain, for example sample PVC/Na3/DEG/IDP achieves 5% decreasing than 148% decreasing of sample PVC/Na5/DEG/ID comparing to pure PVC compound. In additionally, using PEG as intercalation agent (i.e. -5%) leads to also considerable enhancement permeability values than DEG (i.e. 175%) comparing to unfilled PVC compound.

As Table 9 in Appendix shows, from permeability values cannot be expressed concrete result, because those are similar. Only addition of intercalation and co-intercalation agents to nanocomposite system leads to enhancement of barrier properties.

In spite of, the commercial membranes show noticeably worse permeability values than our unfilled PVC compound.

7.2 Solvent resistance

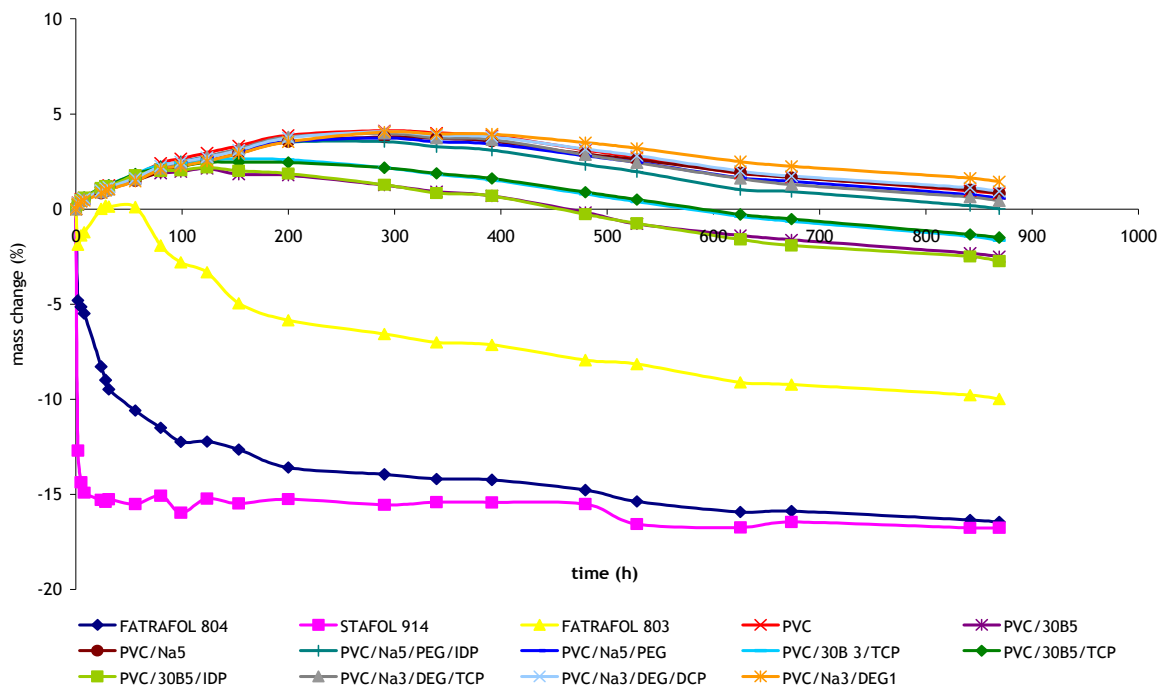


Fig. 20 Weight changes during swelling as a function of time

The materials with the slightest x-axis deviation prove better solvent resistance, in other words these samples demonstrates least swelling and leaching. We can say, that commercial samples had substantially different behaviour than the others as can be seen in Fig. 20. On the other hand, Fig. 20 shows that materials PVC/30B/IDP and PVC/30B have significantly lower degree of swelling than the others and additionally materials PVC/30B3/TCP and PVC/30B/TCP show also lower degree of leaching in comparison with PVC/30B/IDP and PVC/30B. After certain period soluble matter was eluted in all samples. However, as can be seen, the eluting of almost all nanocomposite materials was retarded to materials containing Cloisite® 30B. The best soluble resistance could be characterized by depending on utilization, in other word nanocomposites containing Cloisite® 30B can be used for short-time applications (to 500 hours).

The FTIR was preformed to study structural changes. Both solvent – octane and samples were examined. As Fig. 22 shows, FTIR spectra of pure octane are not different than the

FTIR spectra of octane, in which samples were swelled. This characteristic is similar for all octanes.

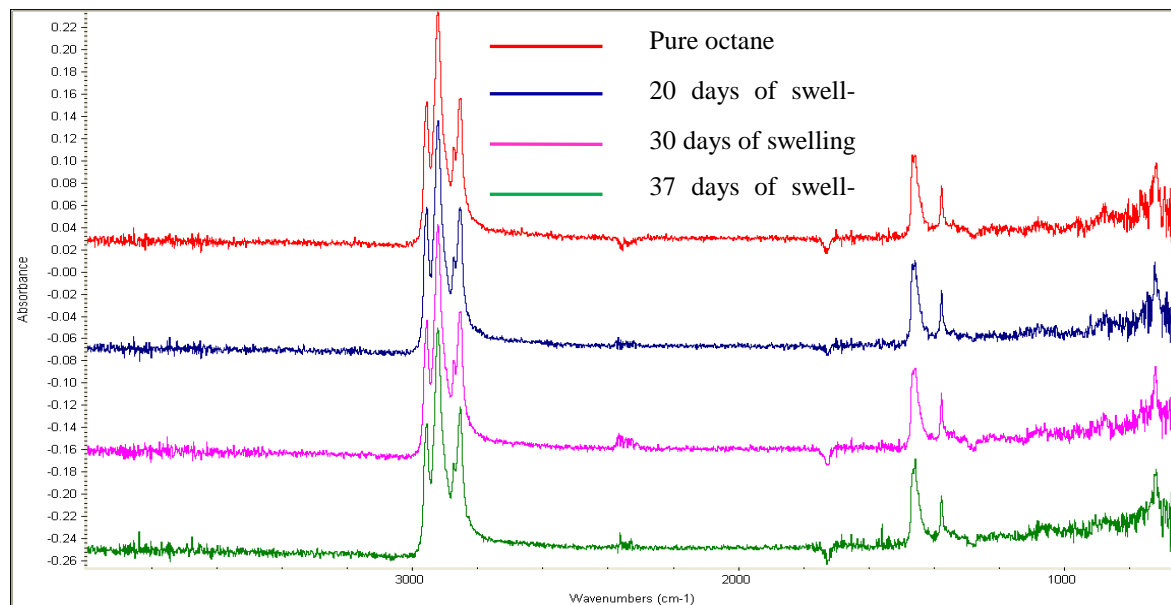


Fig. 21 FTIR spectra of octane, in which PVC samples were swelled

Figures 22 and 23 should illustrate structural changes between the materials with poor (PVC/Na3/DEG) and with good (PVC/30B5/IDP) solvent resistance. Visible changes were erased in wavenumber area 1030 -1100 cm⁻¹ characterized as C-Cl boundary. It is obvious by comparing of these two samples, in more swelling PVC/Na3/DEG 1 these peaks are missing.

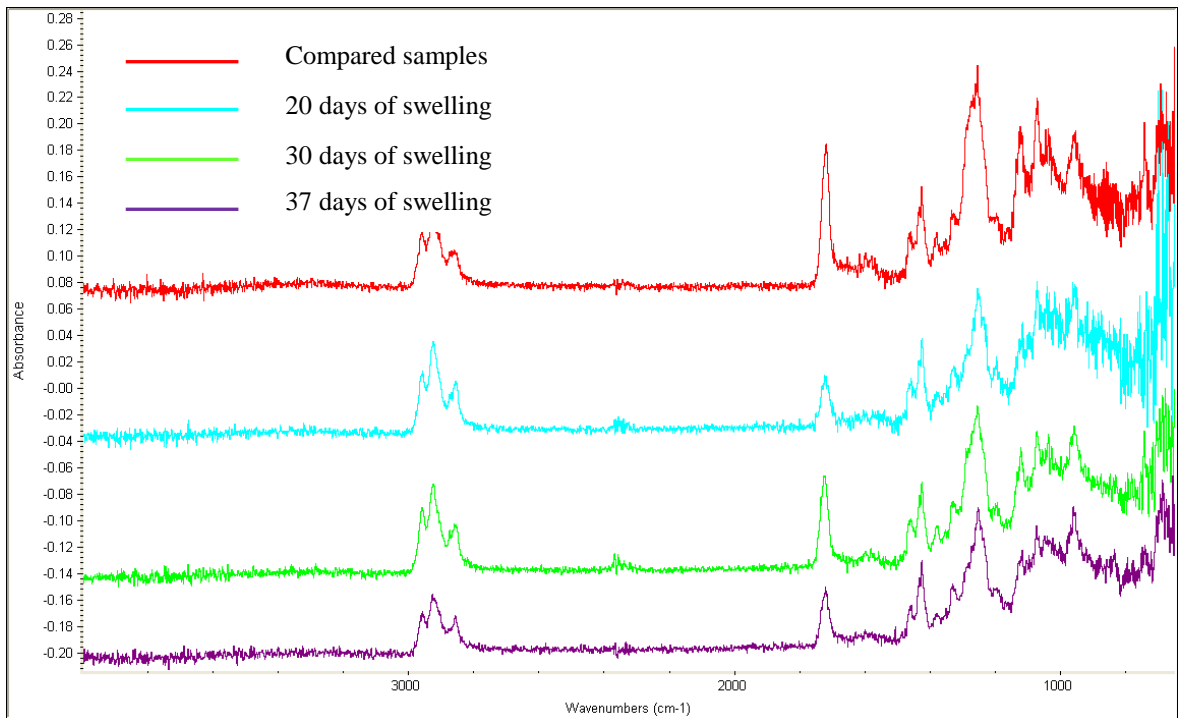


Fig. 22 FTIR spectra of PVC/Na3/DEG 1 during swelling

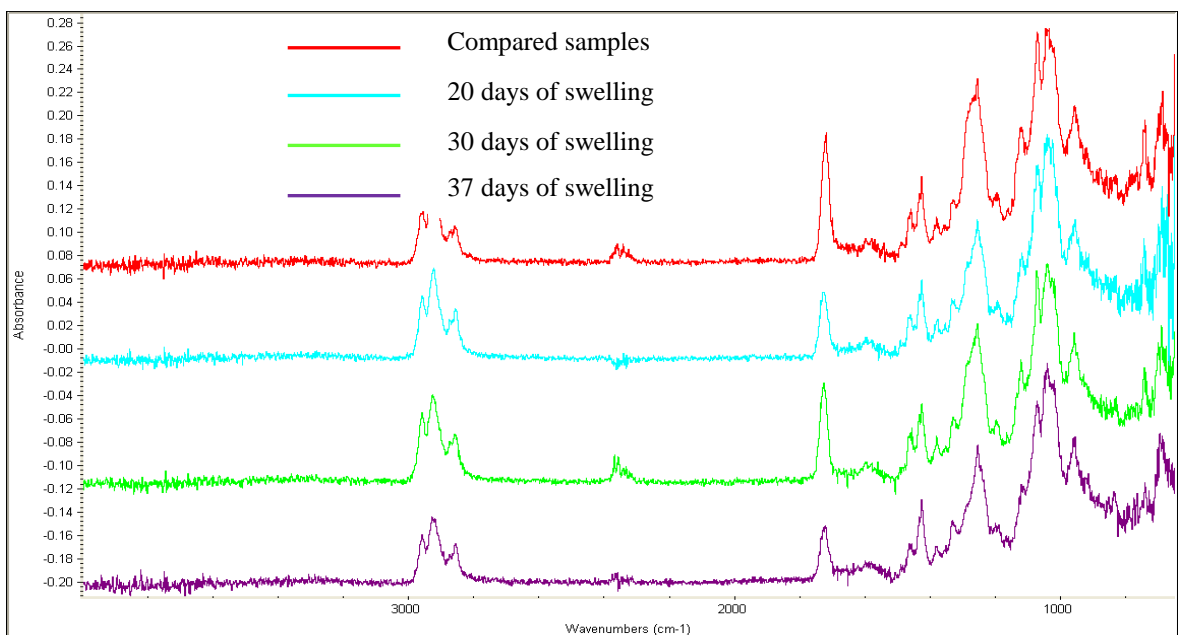


Fig. 23 FTIR spectra of PVC/30B5/IDP

In summary, all measured values (see Table 10 in Appendix) shown in Fig. 25 were affirmed conclusion mentioned above.

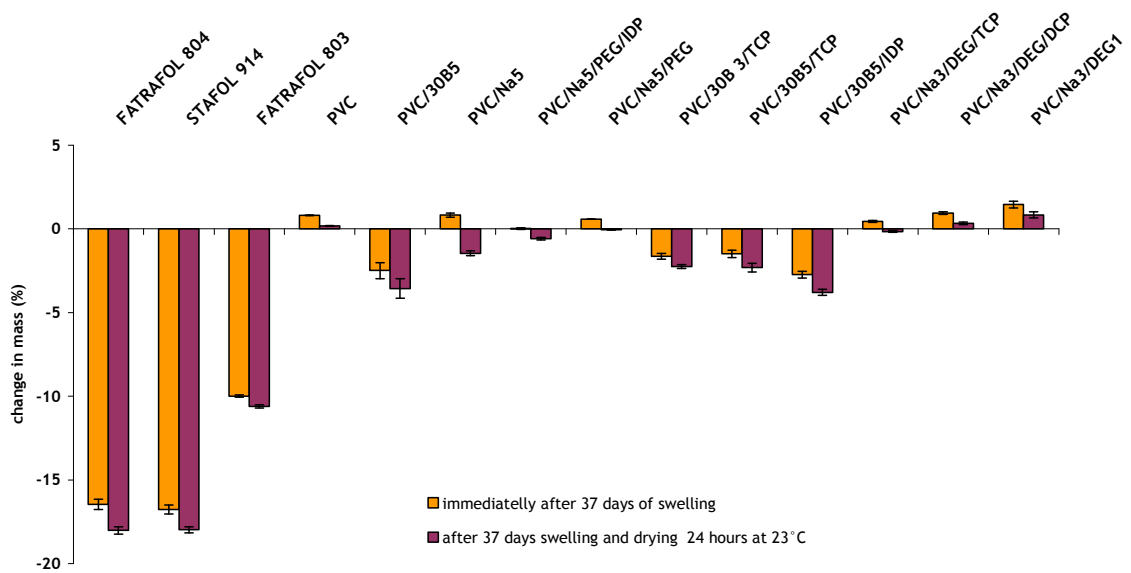


Fig. 24 Weight changes of samples before and after drying

7.3 Determination of water content

This method is suggested for determining the moisture absorption properties in through-the-thickness direction of flat solid plastics. The water-sorption behaviour of nanocomposite samples and commercial membranes during 1 week at 23°C were plotted in Fig. 25. All these samples showed a linear initial uptake, although there are some scatters probably caused by un-accurate measuring. At the first point of view, one could describe that low water content have unfilled PVC compound and commercial membranes (FATRAFOL 803 and 804), but this note were disproved by diffusion coefficient in Table 4.

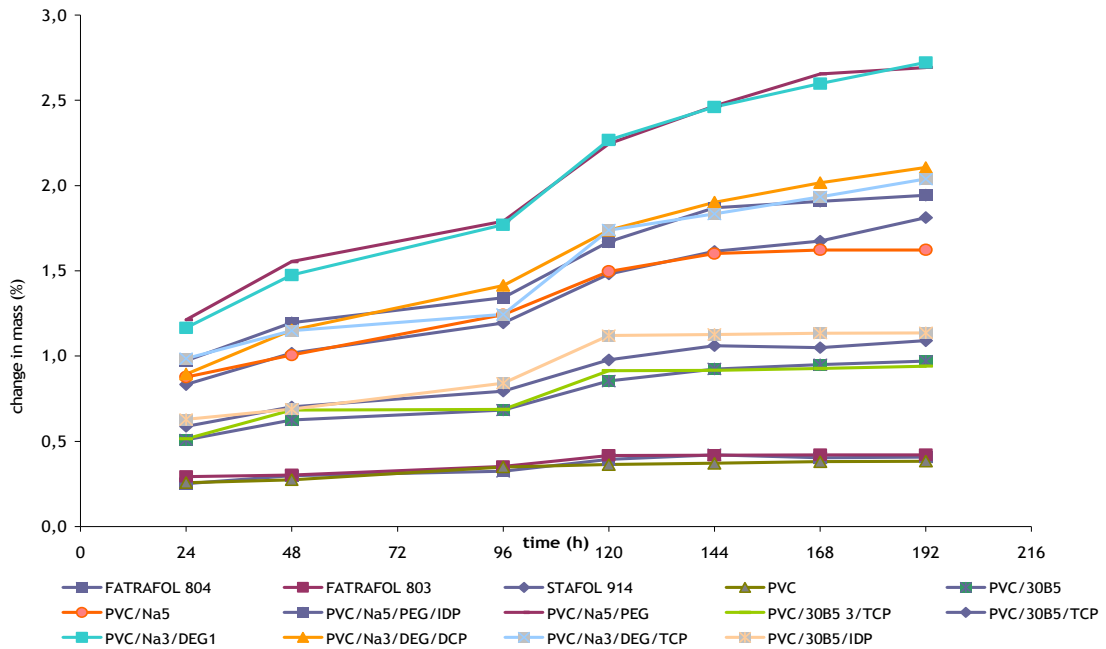


Fig. 25 Determination of water-soluble matter lost during immersion in water at 23°C

The diffusivity data of nanocomposites calculated according to the Fick 's law (equation 10) are presented in Table 4.

Table 4 Calculated values of moisture diffusivity and equilibrium moisture content of prepared samples and commercial membranes

system	c (%) ⁴	Diffusion Coefficient x 10 ¹⁴ (m ² /s)	c _s (%) ⁵
FATRAFOL 804	0,41	225,56	0,36
FATRAFOL 803	0,42	15,32	0,64
STAFOL 914	0,41	36,74	1,30
PVC	0,38	17,85	0,38
PVC/30B	0,97	2,95	1,10
PVC/Na5	1,62	39,25	1,63
PVC/Na5/PEG/IDP	1,94	1,68	2,50
PVC/Na5/PEG	2,69	57,45	2,70
PVC/30B 3/TCP	0,94	3,66	1,09
PVC/30B5/TCP	1,09	11,95	1,12
PVC/30B5/IDP	1,14	19,47	1,14
PVC/Na3/DEG/TCP	2,04	0,80	4,80
PVC/Na3/DEG/DCP	2,11	7,65	2,40
PVC/Na3/DEG1	2,72	3,26	3,58

The low value of Diffusion coefficient, which should be explained by tortuous path hypothesis, were occurred in materials PVC/Na3/DEG /TCP, PVC/Na5/PEG/IDP and surprisingly PVC/30B5. Sample PVC/Na3/DEG/TCP show considerably higher water content of saturation with lower diffusion coefficient than unfilled PVC compound (see also Fig. 27). In additionally, it could be suggested that the addition of DEG as intercalation agent leads to lower diffusion coefficient than using PEG (with some differences).

⁴ Percentage water content

⁵ Percentage water content at saturation

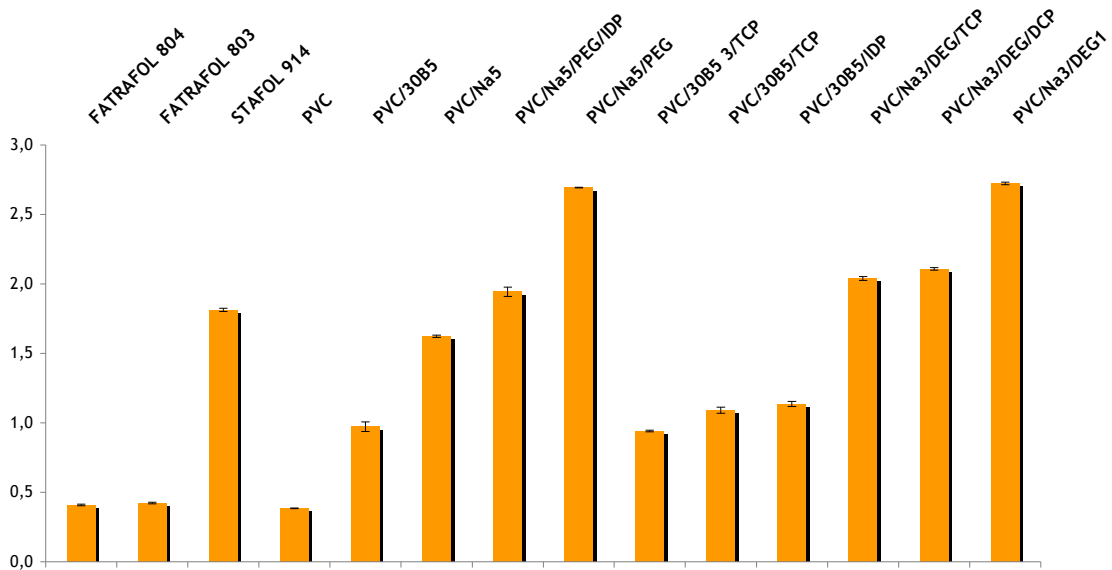


Fig. 26 Determination of water content absorbed after 192 hour immersion in water at 23°C

From different literature we know that the predicted diffusion coefficient should depend sensitively on the physical structure, or equivalently the filler agglomeration level, of the nanocomposite; in particular, there should be a substantial difference in the diffusion coefficient when the clay is exfoliated compared to when it is intercalated. Unfortunately, these differences cannot be picked up in sorption experiments when the diffusing molecule, such as distilled water, adsorbs significantly onto the clay surface, and the amount of adsorbed moisture is comparable to or more than the amount of moisture that can be dissolved in the polymer. When moisture enters the nanocomposite, it is attracted to the clay surface, and water molecules preferentially go to the surface of the clay platelets that they encounter first before diffusing further into the polymer. This is functional only when the surface of these filler particles is completely saturated with moisture [35].

This Fig. 27 illustrated (see values in Table 11 in Appendix), that nearly all samples have greater water-soluble matter lost than unfilled PVC compound. Only PVC/Na5 and PVC/Na3/DEG/TCP offered markedly lower matter lost than others.

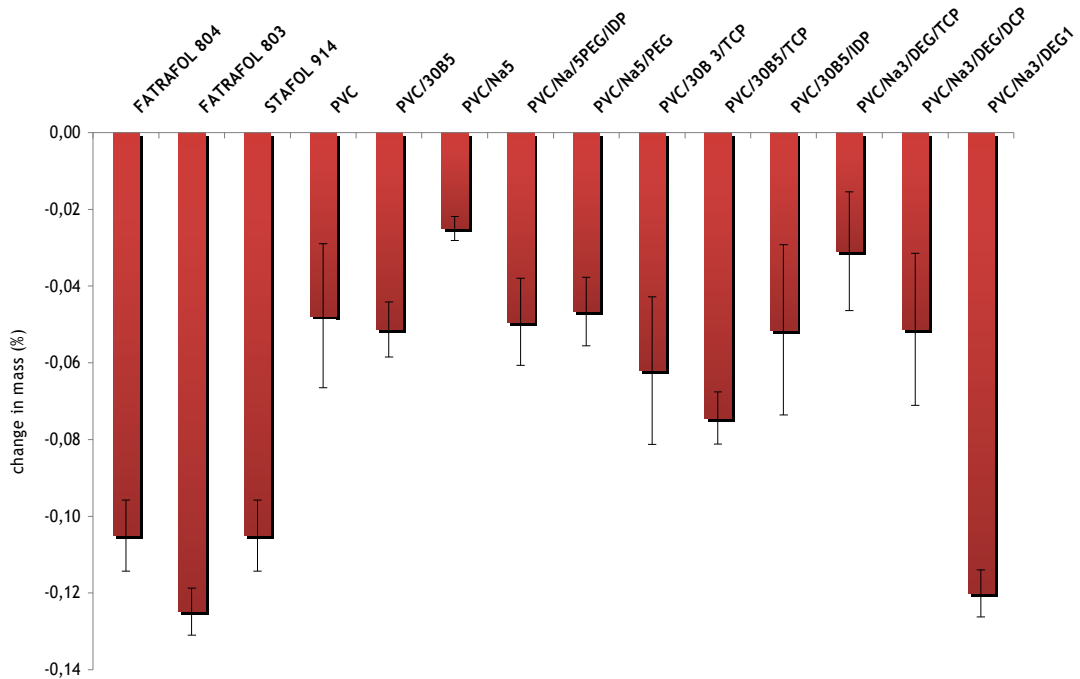


Fig. 27 Determination of water-soluble matter lost during immersion in water at 23°C

All samples were also exposed to 50% relative humidity and water content absorption was determined in the similar way like the immersion in water at 23°C. But any changes should not be seen. It could be said that were completely saturated.

Water content after immersion in boiling water was also studied. Results of sorption experiments conducted at boiling water were essentially similar to the results of exposing at 23°C (see Fig. 28).

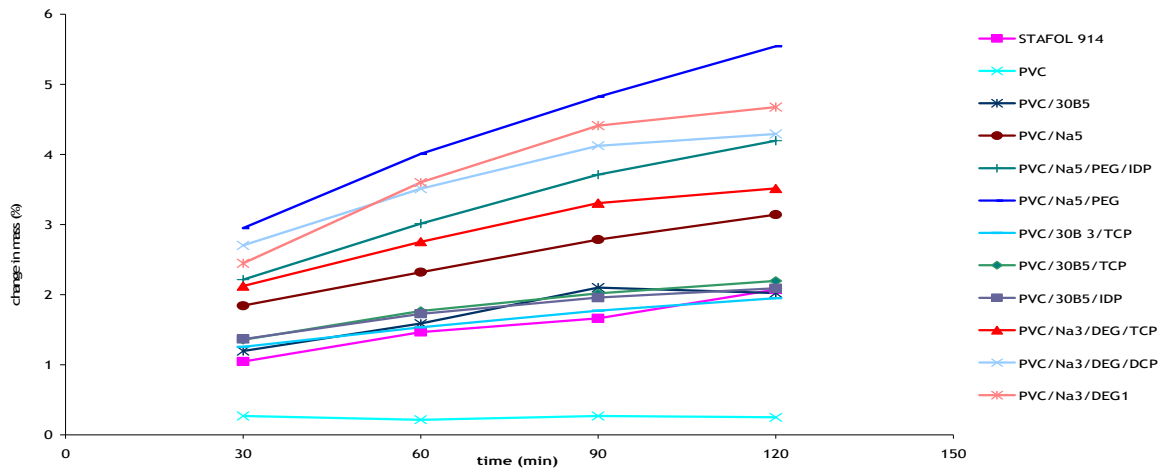


Fig. 28 Time dependence on water content absorbed after 2 hour immersion in boiling water

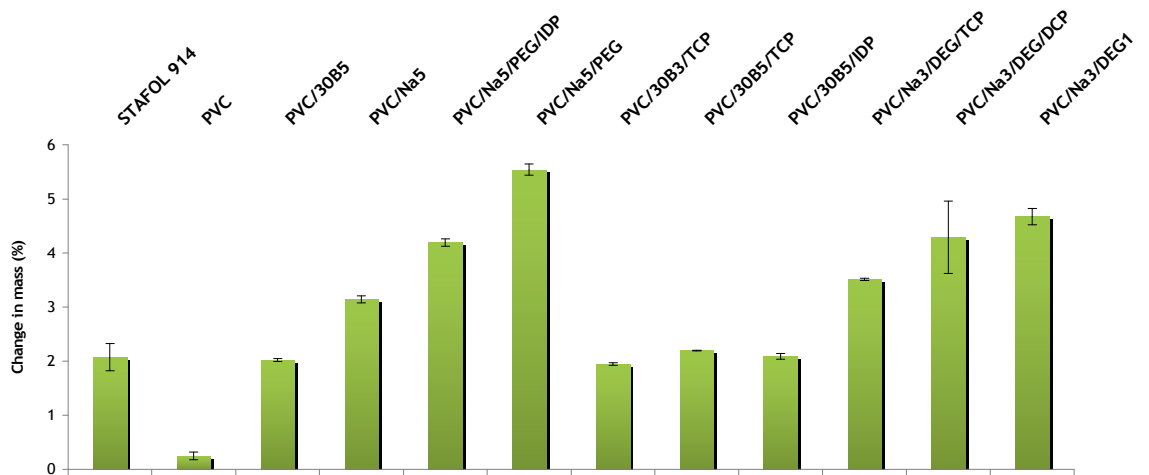


Fig. 29 Determination of water content absorbed after 2 hour immersion in boiling water

As should be seen in Fig. 28 and 29, unfilled PVC compound absorbed low content of water after it are followed both nanocomposite samples with addition of Cloisite® 30B and STAFOL 914.

7.4 Exposure to liquid chemical within water

Experiments, similar to those conducted using distilled water, were also carried out using 0.1 M NaCl solution. Results of the sorption of brine on time dependence were similar to results of moisture sorption.

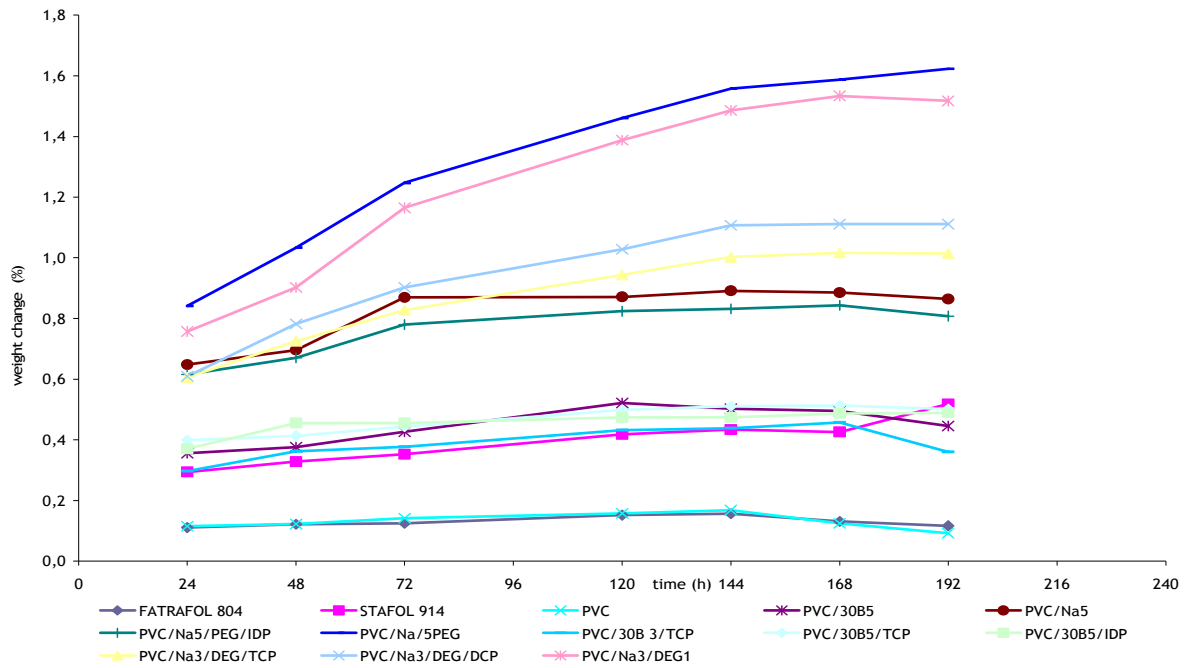


Fig. 30 Weight change of samples during exposing in 0.1 M NaCl solution as a function of time

Table 5 Measured and calculated values of brine (0.1 M NaCl) diffusivity and equilibrium weight gain of prepared samples and commercial membranes

system	c (%)	Diffusion Coefficient x 10^{14} (m ² /s)	c _s (%)
STAFOL 914	0,41	7,04	0,52
FATRAFOL 804	0,12	916,00	0,16
FATRAFOL 803	0,08	35,54	0,16
PVC	0,09	11,83	0,19
PVC/30B5	0,45	0,57	1,80
PVC/Na5	0,86	25,02	0,89
PVC/Na5/PEG/IDP	0,81	0,22	1,90
PVC/Na5/PEG	1,62	10,73	1,67
PVC/30B 3/TCP	0,36	11,13	0,47
PVC/30B5/TCP	0,50	38,27	0,52
PVC/30B5/IDP	0,49	5,77	0,51
PVC/Na3/DEG/TCP	1,01	3,92	1,02
PVC/Na3/DEG/DCP	1,11	13,37	1,25
PVC/Na3/DEG1	1,52	19,64	1,56

When one compares the result presented in Table 4 with those given in Table 5, one notice that clay is much less effective in reducing the diffusivity of brine than distilled water, and brine is adsorbed to a much lesser extent on the clay particles. These expectations are similar as in Rana's research [35].

As further Figures 31 and 32 show, differences between percentage areal weight change and percentage weight change are minimal. It could be say that materials containing nano-filler Cloisite® 30B performed the best resistance to sorption of brine than .

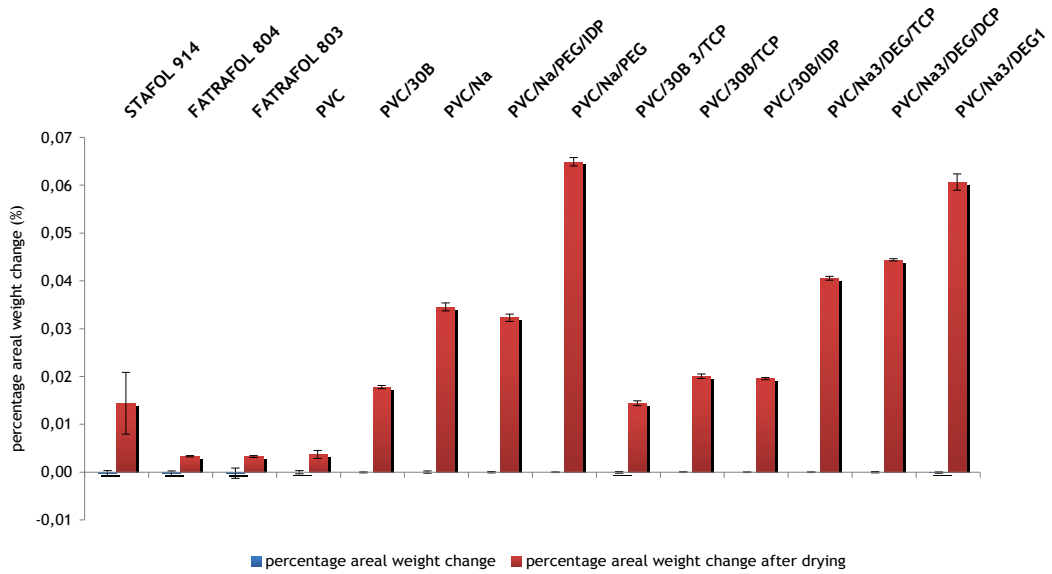


Fig. 31 Percentage areal weight change before and after drying

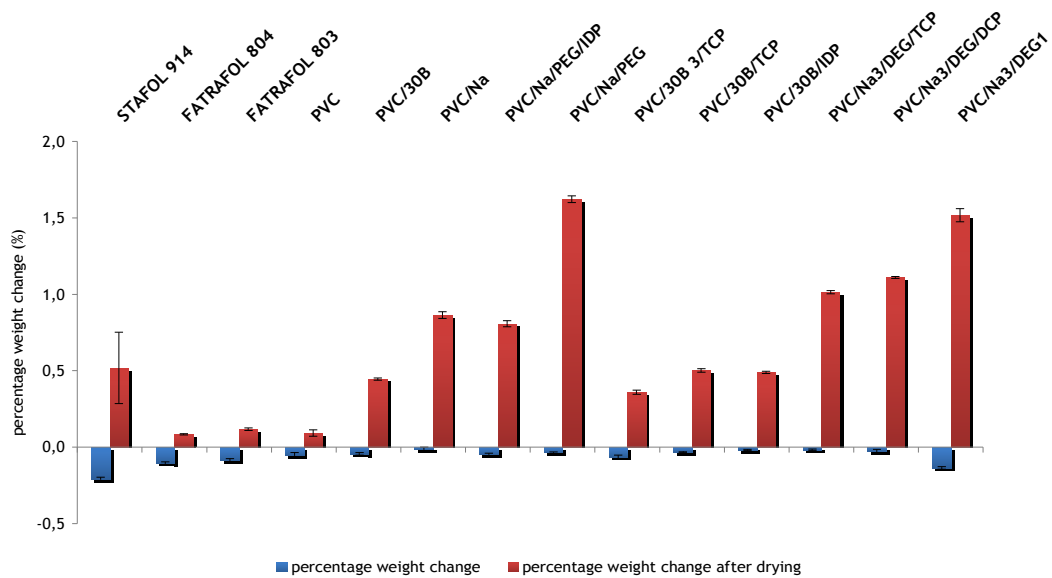


Fig. 32 Percentage weight change during exposing before and after drying

CONCLUSION

Significant progress in the development of polymer/clay nanocomposites has been made over the past one and a half decades.

Clay was chosen as filler due to its low loading range. The ability of clays to organize and direct polymer nanocomposites synthesis comes from a number of unique structural and chemical properties. From the smectite group, the best known and widely utilized clay is montmorillonite.

There are many articles with information about improving barrier properties by adding nanofillers. It is necessary to check this theory practically.

Because of this PPVC was chosen as polymer matrix. It is an example of common plastics material with good barrier properties as a pure material. In fact, the research of barrier properties of PVC/clay nanocomposites has only begun.

Nanocomposite samples with two types of fillers, namely Cloisite® Na⁺ and Cloisite® 30B, were prepared using different amount of intercalation and co-intercalation agents. Then, these samples were compared with commercial membranes.

In present work, barrier properties using Permeability, WVTR, Diffusion coefficient and mass changes at saturation were determined by measuring the changes in weight. It was found out that our prepared samples have significantly better barrier properties than commercial membranes. Generally it could be said, the addition of Cloisite® 30B and subsequent co-intercalation lead to the better barrier properties, namely permeability decreased about 23% by Water method and 70% by Desiccant method. Permeation experiments are thus preferable to sorption experiments, and these might even be used to estimate effectiveness of a given processing techniques to exfoliate platelets.

It could be also said, that enhancement of barrier properties was achieved using only 3wt% of nanofiller. From comparing diffusion coefficients of some materials in different solutions could be found out that increasing diffusion coefficient value was corresponded with reducing mass change at saturation. This result could be explained based on the hydrophilic nature of the clay surface that tends to immobilize some of the moisture. Moreover it could be deduced that materials with 3wt% nanofiller content had lower diffusion coefficient than with 5wt%.

It is necessary to note that barrier properties depend on type of nanofiller, using intercalation and co-intercalation agents and on intercalation/exfoliation degree of nanofiller in polymer matrix.

At the end, we could suggest, that new types of materials utilized as insulation membranes were found.

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LIST OF USED SYMBOLS AND ABBREVIATIONS

PCN	Polymer/clay nanocomposites
XRD	X-ray diffraction
CEC	Cation exchange capacity
PVC	Poly(vinyl chloride)
PA 6	Polyamide 6
PE	Polyethylene
PET	Polyethyleneterephthalate
PP	Polypropylene
PEO	Polyethyleneoxide
PS	Polystyrene
UPVC	Non-plasticized polyvinyl chloride
PPVC	Plasticized polyvinyl chloride
MMT	Montmorillonite
P	Permeability
S	Solubility
D	Diffusivity
Δp	Vapour pressure difference
G/t	Slope of the straight line
S	Saturation vapour pressure at test temperature
R_1, R_2	Relative humidity at the source and at the vapour sink
A	Test area
t	Time
WVT	Water vapour transmission rate
G	Weight change

B_m	Change of weight
m_0	Weight of samples before measurement
m_1	Weight of samples after time t
c	Water content
m_1	Mass of the test specimen after initial drying and before immersion
m_2	Mass of the test specimen after immersion
m_3	Mass of the test specimen after initial drying and final drying
M_t	Mass gain at reduced time
M_∞	Maximum mass gain at the equilibrium state
c_s	Water content at saturation
t	time of immersion of the test specimen in water or humid air

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APPENDIX

Table 6 Calculated data of water vapour transmission method after 1 day using Water method

system after 24 hours	WVT [g/h.m ²]	Δ	%	P [g/Pa.s.m]	Δ	%
PVC/Na5/DEG0.5	58,01	53,50	583,15	4,48E-10	4,29E-10	484,35
PVC/Na3/DEG0.5	3,68	1,35	-56,61	3,09E-11	1,16E-11	-59,65
PVC/Na5/DEG1	9,00	8,09	6,03	8,22E-11	7,37E-11	7,23
PVC/Na3/DEG1	7,63	5,14	-10,21	7,46E-11	5,36E-11	-2,63
PVC/Na5/DEG/DCP	4,02	0,50	-52,64	3,80E-11	5,24E-12	-50,36
PVC/Na3/DEG/DCP	1,79	0,34	-78,92	1,37E-11	3,41E-12	-82,06
PVC/Na5/DEG0,5/TCP	3,09	1,02	-63,64	3,01E-11	1,02E-11	-60,71
PVC/Na3/DEG0,5/TCP	23,45	30,10	176,08	2,73E-10	3,48E-10	256,71
PVC/Na5/DEG/TCP	3,23	1,84	-61,96	3,73E-11	2,07E-11	-51,28
PVC/Na3/DEG/TCP	2,07	1,38	-75,59	2,02E-11	1,30E-11	-73,60
PVC/Na5/DEG/IDP	33,07	22,50	289,41	3,98E-10	2,72E-10	419,40
PVC/Na3/DEG/IDP	2,04	0,23	-75,99	2,02E-11	1,98E-12	-73,64
PVC/Na5/PEG	3,24	1,22	-61,80	3,86E-11	1,37E-11	-49,58
PVC/Na5/PEG/DOP	7,83	2,26	-7,81	7,75E-11	2,53E-11	1,17
PVC/Na5/PEG/TCP	4,27	2,50	-49,71	4,23E-11	2,48E-11	-44,74
PVC/Na5/PEG/IDP	6,77	2,82	-20,27	4,98E-11	2,05E-11	-34,97
PVC/Na5	10,56	7,97	24,33	9,17E-11	6,71E-11	19,71
PVC/30B5	3,57	1,78	-58,02	3,14E-11	1,54E-11	-59,07
PVC/30B5/IDP	6,01	4,17	-29,26	5,88E-11	4,32E-11	-23,20
PVC/30B5/TCP	2,80	1,67	-67,07	2,95E-11	1,74E-11	-61,48
PVC/30B 3/TCP	2,17	1,76	-74,39	2,28E-11	1,86E-11	-70,26
PVC/IDP	2,72	1,74	-67,92	2,65E-11	1,89E-11	-65,41
PVC/TCP	5,36	3,10	-36,86	5,30E-11	3,20E-11	-30,86
FILM 902	0,96	0,19	-88,74	7,80E-12	1,37E-12	-89,82
Blood can	0,64	0,09	-92,45	2,08E-11	2,69E-12	-72,84
FATRAFOL 803	0,81	0,67	-90,41	8,44E-11	6,96E-11	10,12
STAFOL 914	0,48	0,11	-94,39	2,52E-11	3,93E-13	-67,15
PVC	8,49	6,66	0,00	7,66E-11	6,16E-11	0,00

Table 7 Calculated data of water vapour transmission method after 1 month using Water Method

system after 1 month	WVT [g/h.m ²]	Δ	%	P [g/Pa.s.m]	Δ	%
PVC/Na5/DEG0.5	2,67	1,76	251,91	2,04E-11	1,42E-11	206,65
PVC/Na3/DEG0.5	1,24	0,53	63,30	1,02E-11	3,86E-12	53,81
PVC/Na5/DEG1	2,02	1,76	166,48	1,83E-11	1,61E-11	175,15
PVC/Na3/DEG1	0,71	0,16	-6,04	6,81E-12	1,19E-12	2,53
PVC/Na5/DEG/DCP	0,86	0,08	13,92	8,14E-12	5,84E-13	22,57
PVC/Na3/DEG/DCP	0,89	0,08	17,94	6,74E-12	1,44E-13	1,47
PVC/Na5/DEG0,5/TCP	0,84	0,15	10,34	8,13E-12	1,47E-12	22,45
PVC/Na3/DEG0,5/TCP	0,65	0,11	-13,69	8,30E-12	2,07E-12	25,02
PVC/Na5/DEG/TCP	0,65	0,07	-14,69	7,66E-12	6,12E-13	15,43
PVC/Na3/DEG/TCP	0,67	0,07	-11,35	6,67E-12	5,16E-13	0,42
PVC/Na5/DEG/IDP	1,37	0,46	81,08	1,64E-11	5,72E-12	147,81
PVC/Na3/DEG/IDP	0,70	0,12	-7,00	6,97E-12	1,08E-12	5,04
PVC/Na5/PEG	0,54	0,09	-28,25	6,29E-12	8,04E-13	-5,23
PVC/Na5/PEG/DOP	1,35	0,89	78,22	1,22E-11	8,43E-12	83,26
PVC/Na5/PEG/TCP	0,72	0,19	-4,58	7,16E-12	1,84E-12	7,87
PVC/Na5/PEG/IDP	0,87	0,11	14,83	6,37E-12	5,81E-13	-4,07
PVC/Na5	0,81	0,29	7,37	7,25E-12	2,59E-12	9,25
PVC/30B5	0,73	0,10	-3,21	6,46E-12	8,16E-13	-2,67
PVC/30B5/IDP	0,52	0,01	-30,80	4,60E-12	8,09E-13	-30,76
PVC/30B5/TCP	0,52	0,09	-31,60	5,48E-12	9,48E-13	-17,50
PVC/30B 3/TCP	0,51	0,07	-32,46	5,31E-12	7,15E-13	-20,05
PVC/IDP	0,83	0,17	9,83	7,88E-12	2,07E-12	18,69
PVC/TCP	1,23	1,08	62,10	1,19E-11	1,07E-11	79,81
FILM 902	1,49	0,33	96,70	1,22E-11	2,78E-12	84,32
Blood can	0,47	0,05	-37,33	1,54E-11	1,74E-12	132,31
FATRAFOL 803	0,56	0,59	-25,90	5,81E-11	6,12E-11	775,89
STAFOL 914	0,43	0,17	-43,31	2,69E-11	1,07E-11	305,21
PVC	0,76	0,08	0,00	6,64E-12	1,09E-12	0,00

Table 8 Calculated data of water vapour transmission method after 1 day using Desiccant method

system after 24 hours	WVT [g/h.m ²]	Δ	%	P [g/Pa.s.m]	Δ	%
PVC/Na3/DEG1	0,45	0,21	73,42	3,84E-12	1,62E-12	-24,20
PVC/Na3/DEG/DCP	0,28	0,01	8,70	2,36E-12	1,28E-13	-53,52
PVC/Na3/DEG/TCP	0,25	0,05	-1,38	2,50E-12	4,18E-13	-50,67
PVC/30B5/IDP	0,15	0,05	-42,66	1,69E-12	5,48E-13	-66,65
PVC/30B5/TCP	0,16	0,06	-35,99	1,58E-12	6,03E-13	-68,77
PVC/30B 3/TCP	0,19	0,13	-25,17	1,71E-12	1,13E-12	-66,29
PVC/Na5/PEG	0,17	0,08	-33,27	1,92E-12	9,15E-13	-62,08
PVC/Na5/PEG/IDP	0,36	0,07	41,66	2,96E-12	1,50E-13	-41,72
PVC/Na5	0,43	0,10	65,27	3,67E-12	8,70E-13	-27,68
PVC/30B5	0,26	0,19	2,17	9,48E-12	6,85E-12	86,94
FILM 902	0,36	0,03	38,77	2,86E-12	1,43E-13	-43,52
Blood can	0,12	0,04	-54,91	3,76E-12	1,45E-12	-25,84
FATRAFOL 803	0,22	0,09	-13,39	1,31E-11	5,43E-12	158,03
STAFOL 914	0,26	0,02	0,64	1,22E-11	1,34E-12	139,72
PVC	0,26	0,12	0,00	5,07E-12	2,45E-12	0,00

Table 9 Calculated data of water vapour transmission method after 1 month using Desiccant Method

system after 1 month	WVT [g/h.m ²]	Δ	%	P [g/Pa.s.m]	Δ	%
PVC/Na3/DEG1	0,57	0,15	28,18	5,00E-12	1,01E-12	-42,92
PVC/Na3/DEG/DCP	0,45	0,02	1,33	3,82E-12	2,86E-13	-56,45
PVC/Na3/DEG/TCP	0,36	0,03	-18,41	3,60E-12	2,70E-13	-58,95
PVC/30B5/IDP	0,22	0,03	-49,89	2,59E-12	2,55E-13	-70,48
PVC/30B5/TCP	0,26	0,06	-42,24	2,47E-12	5,63E-13	-71,81
PVC/30B 3/TCP	0,29	0,08	-35,51	2,62E-12	5,72E-13	-70,11
PVC/Na5/PEG	0,32	0,04	-28,48	3,58E-12	4,43E-13	-59,21
PVC/Na5/PEG/IDP	0,53	0,05	17,71	4,45E-12	9,85E-13	-49,30
PVC/Na5	0,53	0,08	19,50	4,60E-12	7,02E-13	-47,52
PVC/30B5	0,20	0,03	-56,19	7,11E-12	1,08E-12	-18,95
FILM 902	0,60	0,01	33,60	4,80E-12	2,13E-13	-45,28
Blood can	0,31	0,03	-29,70	1,01E-11	9,90E-13	15,60
FATRAFOL 803	0,22	0,09	-50,12	2,31E-11	8,98E-12	162,93
STAFOL 914	0,26	0,02	-42,04	1,62E-11	1,54E-12	84,22
PVC	0,45	0,14	0,00	8,77E-12	2,92E-12	0,00

Table 10 Calculated data of solvent resistance method

system	B_0 [%] after 37 days	Δ	B_0 [%] after drying	Δ
FATRAFOL 804	-16,4550	0,3194	-18,0052	0,2177
STAFOL 914	-16,7534	0,2700	-17,9719	0,1801
FATRAFOL 803	-9,9873	0,0760	-10,6025	0,0963
PVC	0,8118	0,0240	0,1735	0,0224
PVC/30B5	-2,4907	0,4754	-3,5607	0,5799
PVC/Na5	0,8208	0,1242	-1,4536	0,1485
PVC/Na5/PEG/IDP	0,0155	0,0504	-0,5882	0,0695
PVC/Na5/PEG	0,5698	0,0059	-0,0523	0,0207
PVC/30B 3/TCP	-1,6459	0,1736	-2,2602	0,1117
PVC/30B5/TCP	-1,4980	0,2214	-2,3215	0,2554
PVC/30B5/IDP	-2,7357	0,1962	-3,7999	0,1831
PVC/Na3/DEG/TCP	0,4380	0,0586	-0,1689	0,0473
PVC/Na3/DEG/DCP	0,9349	0,0816	0,3266	0,0642
PVC/Na3/DEG1	1,4496	0,1929	0,8315	0,1838

Table 11 Calculated water-soluble matter lost during immersion at 23°C

system	Δm (%) after 8 days	Δ
FATRAFOL 804	-0,1051	0,0093
FATRAFOL 803	-0,1249	0,0062
STAFOL 914	-0,1051	0,0093
PVC	-0,0477	0,0188
PVC/30B	-0,0513	0,0072
PVC/Na	-0,0250	0,0031
PVC/Na/PEG/IDP	-0,0493	0,0113
PVC/Na/PEG	-0,0466	0,0089
PVC/30B 3/TCP	-0,0620	0,0192
PVC/30B/TCP	-0,0744	0,0068
PVC/30B/IDP	-0,0514	0,0222
PVC/Na3/DEG/TCI	-0,0309	0,0155
PVC/Na3/DEG/DCI	-0,0513	0,0198
PVC/Na3/DEG1	-0,1201	0,0061