Polymerní speciální a multifunkční folie

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Teze disertační práce

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Doctoral Thesis Summary

Polymerní speciální a multifunkční folie

Polymer Special and Multifunctional Films

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ABSTRAKT

Předložená doktorská práce je zaměřena na přípravu, vlastnosti a využití polymerních speciálních a multifunkčních folií. Je zde nastíněna problematika přípravy a zlepšení některých vybraných vlastností, jako například mechanických a bariérových. Polymerní folie však nejsou nutně jen bariérové a mnohé z nich nalezneme nejen v potravinářském průmyslu, ale i v jiných oblastech průmyslové výroby. Doktorská práce se tedy věnuje nejen foliím s vylepšenými bariérovými vlastnostmi, ale i foliím vyrobeným z recyklovaného materálu.

Disertační práce se skládá ze dvou částí. Teoretická část je věnována stručnému popisu polymerních, vícevrstvých, multifunkčních folií a použitým polymerním matricím ze skupiny polyolefinů, jejich kopolymerů a vinylových polymerů. V práci jsou také popsány výrobní postupy a metody použité k hodnocení vybraných vlastností folií. Hlavní pozornost je věnována nanoplnivům a jejich použití v polymerních foliích.

Druhá část práce předkládá výsledky získané během doktorského studia formou krátkého shrnutí jednotlivých publikovaných článků. Výzkumné práce v plném znění jsou k dispozici v samém závěru práce.

ABSTRACT

Doctoral thesis is focused on preparation, properties and utilization of polymer special and multifunctional films. Issues of preparation and enhancement of selected properties, such as mechanical or barrier, are outlined. However, polymer films are not necessarily applied only as barriers. A variety of them may be emploed in the the food industry or in the other areas of industrial production as well. Therefore, doctoral thesis focuses not only on films with improved barrier properties, but also on films produced from recycled materials.

Thesis is divided into two main parts. Theoretical part is devoted to brief description of polymeric, multilayer, multifunctional films and applied polymer matrices from the group of polyolefins, their copolymers and vinyl polymers. The paper also describes manufacturing processes and methods used to evaluate selected film properties. Major focus is placed on nanoparticles and their application in polymeric films.

The second part presents the results obtained during the doctoral study in the form of a short summary of published articles. Full-text research is to be seen at the end of the paper.

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CONTENT

INTRODUCTION

THE CURRENT STATE OF THE TOPIC

Special and multifunctional polymer films have become well-established in many types of manufacturing industries. Polymer films are predominantly used as packaging materials, some may be even applied as auxiliary materials in the industry. Although plastics are not the only packaging material, they have gradually replaced more traditional packaging materials, such as metal, glass and wood. It has been estimated that approximately 75 % of all films produced in Europe are used in the packaging industry [1].

Polymeric films usage is associated with product protection against the climatic influences, aggressive gases and aerosols, against the UV radiation, oils, fats, acids and bases, but also against microbial attacks. Not surprisingly, the food industry is one of significant consumers of polymer films. Film materials from polyolefins and their copolymers, polyesters, polyamides, polystyrene and vinyl polymers are those the most used due to their specific properties [2].

Application of fillers into polymer films provides additional possibilities to enhance the properties of packaging materials. Especially nanoparticles in polymeric matrix can substantially improve some of the properties and consequently the properties of the final product films, even with the minimum of nanofibre content. If matrix is formed by polymer component and filler with at least one dimension in nanoscale, the final product is referred to as a nanocomposite. Nanofillers may occur in the form of nanoculars, nanopowders or nanotubes [3, 4].

Clay materials contain nanoparticles in the form of nanopowders and are applied in the plastics and building industry, and also in the ceramics and agriculture.

If nanofibres exfoliation is gained in polymer matrix, clay nanoparticles may significantly affect the properties of prepared polymer, enhance mechanical properties and reduce the gas and water vapor permeability [5, 6].

As it was already mentioned above, polymeric films may not necessarily act only as a barrier, but may also be used as waterproof films used in the building industry. Individual layers of floor coverings between the foils may be arranged as well. What is more, the alternative to replace some of these multilayer films with recycled materials attracts growing attention. Application of recycled PVB as a possible substitution for PVC in these products appears to be a significant opportunity to reduce the amount of these waste materials in landfills [7, 8].

1 AIMS OF THE DOCTORAL THESIS AND THEIR FULFILMENT

The aim of the doctoral thesis is to prepare polymer special multifunctional films.

Partial aims of the work include:

- *Research of polymer materials* – this goal has been achieved.

Various types of polymeric matrix and clay nanoparticles were selected in the first part of the thesis. Based on measured properties, particularly barrier and mechanical properties, polyethylene (LDPE) was selected for further detailed testing.

Published as **Mechanical Properties of PE, PP, Surlyn and EVA Clay/Nanocomposites for Packaging Films.**

- *Mapping the possibilities of using prepared polymer films* – this goal has been achieved.

In the next part of the thesis, the attention was attracted to PE foils and their copolymers. For example, EOC copolymer with different octene content was tested.

Results were published as **Ethylene-Octene Copolymers/Organoclay Nanocomposites: Preparation** and **Properties and Influence of Clay Nanofillers on Properties of Ethylene-Octene Copolymers.**

- *Preparation of polymeric films containing nanofibers and waste filler* – this goal has been achieved.

Next part of the work focused on LDPE films containing nanofillers. Possibility of using these foils in the packaging industry was studied. The base film prepared this way was used as one of the layers of a 5-layer film of industrially manufactured foil.

In addition, films have been prepared containing other nanoparticles, such as nano Ag and nano Fe. Polymeric matrix was formed by LDPE.

Co-author of utility model - Multilayer packaging film with antimicrobial effects and method of their production from 14. 12. 2015

Another part of the work has been devoted to polymer blends preparation. This includes materials of similar composites that are well miscible. Results of PVC and PVB mixtures blending will be published as **Basic Properties of PVC/PVB Pure and Recycled Material Blends and Their Preparation.**

Co-author of utility model - Polyvinyl butyral recyclate for the preparation of polymer blends and polymer mixtures containing it from 15. 9. 2016

Co-author of utility model - Universal pad used in construction from 24. 7. 2017

- *Determination of selected evaluation methods for particular types of polymeric films* – this goal has been achieved.

Evaluation methods to characterize properties of special and multifunctional films were selected. Specifically, barrier properties, morphology, mechanical properties, XRD and FTIR for barrier films with nanofillers and mechanical properties and hardness for multifunctional films PVC/PVB.

The purpose of preparing polymeric films is to obtain such a film composition that it would be feasible to manufacture it industrially.

2 THEORETICAL BACKROUND

2.1 Polymer films

Polymeric material films are flat units with a thickness of about 2 μm. Common features of these polymeric films include barrier properties, resistance to high and low temperatures, mechanical resistance, weldability and printability. Properties required by the packaging industry are often impossible to meet by only one specific polymeric material.

A suitable solution is a polymeric film comprising multiple layers of different polymer types providing desired properties, especially barrier ones.

By combining two or more polymers, it is possible to achieve enhanced foil properties, such as tensile and impact strength, ductility and flexibility. Polymeric films are characterised by their chemical composition, the order and thickness of individual layers. A layer in a direct contact with food must suit the properties of health-conscious material, such as PE, PP and EVA. On the other hand, materials as PVC or PVB may be applied for non-food applications. Outer layers must perform certain specific traits, such as resistance against the UV radiation, abrasion and water. Internal adhesive layers, often being referred to as "tie - layers", are mostly ionomers, EVA, EMAA and melamine hydrides in a very thin layer of about 4 g / m². The cost of used polymeric materials is also a very important criterion of the individual film layer choice [5, 9, 10].

2.2 Main materials of polymer films

Carrier materials form a skeleton or the basis of all polymeric films. These include polyethylene, polypropylene, EVA, Surlyn, ethylene-octene copolymer, PVC and PVB.

Polyethylene (PE)

It is the most popular polyolefin produced by ethylene polymerization. It was prepared by heating diazomethane by Hans von Peckmann for the first time in 1898. Nevertheless, the history of polyethylene production dates back to 1935. Until 1953 it was manufactured only in a high-pressure way. In 1953 Ziegler's catalyst was applied to enable polyethylene production at normal pressure [11]. Today, PE is one of the most common packaging materials. Several types of polyethylene have been distinguished differing in the macromolecule structure (chain branching) and density, which is reflected in its properties. Mostly HDPE, LDPE and LLDPE are applied in the packaging industry [12, 13].

Polypropylene (PP)

Discovery of polypropylene is associated with Professor Natta from Polytechnic in Milan in 1954. Special polymerization initiator, known as stereospecific catalyst, was employed to polymerize propylene.

Natt's discovery was closely connected with Professor Ziegler's work on low-pressure ethylene polymerization.

Structural composition of polypropylene influences its resistance at higher temperatures. Softening point of pure polypropylene is 176 °C. Conventional commercial product has a softening point slightly lower, at approximately 165 °C. Polypropylene is also remarkable for its excellent electro-insulating and dielectric properties [14, 15].

Chemical resistance of polypropylene is related to its chemical structure. Polypropylene is insoluble in organic solvents. In chlorinated and aromatic solvents, polypropylene can be dissolved at higher temperatures. Polypropylene is also resistant to acids and alkalis. Addition of stabilizers may prevent unfavourable effects of air oxygen and ozone [16, 17].

Ethylene vinyl acetate copolymer (EVA)

Ethylene vinyl acetate (EVA) is produced by radical copolymerization of branched ethylene (LDPE) with vinyl acetate in a temperature range from 180 to 250 °C and the pressure of 140 MPa. Its crystallinity decreases with an growing vinyl acetate content. That improves toughness, flexibility and adhesion of the material to the heat. Ideal content of vinyl acetate is considered to be up to 20%. In such conditions EVA acquires properties similar to those of softened PVC. EVA is mainly used for the production of stretch and shrinking films, packaging materials, hoses, lacquers, adhesives and may substitute for softened PVC. Films made from EVA copolymer can be welded at the temperatures between 105 and 135 °C. Ethylene vinyl acetate can be dissolved in ketones and aromatic or chlorinated hydrocarbons [15, 16].

Surlyn

DuPont launched Surlyn A, which is a trade name for a copolymer of ethylene with vinylcarboxylic acids, such as methacrylic acid (EMAA) or acrylic acid (EAA) with free carboxyl groups converted to salts derived from metals of groups I or II. It is a flexible polymer with properties similar to polyethylene LDPE. However, these copolymers perform higher strength and toughness, enhanced hot grip and better adhesion to other materials [15].

EOC

In addition to commonly used types of polyolefins, special polymers have also been attracting the attention of the professional public. Ethylene-octene copolymer (EOC) is one of them, suitable particularly for the use in the combination with aforementioned polymers, especially PP. Ethylene-octene copolymer developed by Dow Chemical Company (Delaware, USA) with metallocene catalysts is being recognized thanks to its eminent properties both in the research and industry [4-6]. The presence of octen in EOC comonomer affects the level of crystallinity and provides a greater flexibility. EOC may be considered as polyolefin (POE) and octane content in copolymer typically ranges from 17 to 45 wt. % [18-20].

Polyvinyl chloride (PVC)

PVC is thermoplastic, slightly branched (< 10 branches per molecule) polymer. Chlorine atom in the molecule increases intermolecular attracting forces causing both the stiffness and hardness of the polymer. PVC powder lasts temperatures of 60-65 °C on a long-term basis. It softens at temperatures of about 80 °C and warming above 100 °C causes a slow decomposition together with removing hydrogen chloride (HCl). Stabilizers may cease HCL releasing even at temperatures exceeding 160 °C. PVC properties depend on its viscosity, which is defined by K-value. This value divides PVC into a hard (K = 56-65) and soft type (K = 65-80). The higher K value is, the better mechanical properties of the film are gained, but the worse it could be processed. Plasticized PVC is used to produce waterproofing foils and floor coverings [21, 22].

Polyvinyl butyral (PVB)

PVB is the most significant polymer of polyvinylacetals formed as a condensation product of the reaction of polyvinyl alcohol and aldehydes. Foils made of polyvinylacetals perform an excellent adhesion to metals and glass thanks to hydrophilic vinyl alcohol and vinyl acetate units.

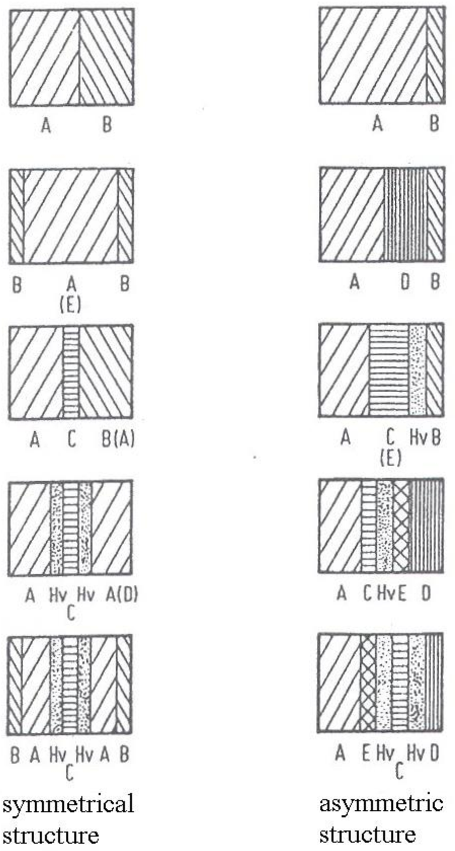
Concerning applications, PVB may be divided into 3 groups - showing low, medium and hight viscosity. High viscosity type is utilized as an adhesive interlayer of safety glasses. Extrusion temperatures reach more than 150 °C. Generated foils are highly plastic and adhesive [23, 24].

2.3 Multilayer films

Characteristics of simple and multilayer barrier films

Common features of polymeric films include barrier properties, resistance to high or low temperatures, transparency, translucency, mechanical resistance, weldability and printability. As mentioned earlier, film properties required by the packaging industry are not often possible to guarantee by only one polymeric material. Polyolefins, polyvinylchloride, polystyrene, polyamides, polyvinyl alcohol and polyesters are used as polymer materials suitable for single (homogeneous) films for both food and non-food applications [5, 25]. *Combining two or more polymeric materials may enhance some properties, such as* tensile and impact strength, ductility, flexibility, chemical and heat resistance, water vapor permeability and processability. Characteristic properties of multi-layered films are defined by their chemical composition and the order and thickness of individual layers. It is necessary to follow certain principles to determine the order of each layer. Layers in a direct contact with food must be produced of non-toxic materials (PE, PP, PETP); on the other hand, materials based on PS, PVC, PVDC may be applied in non-food utilizations. Outer layers must correspond with other specific requirements, such as the resistance against the UV radiation, abrasion, solvents, oils and water. Internal adhesive layers known as "tie - layers" are mostly ionomers, EVA, EMAA and melamine hydrides applied in a very thin layer of about 4 g / m². Economic reasons limit the use of recycled materials in barrier foils only to restricted quantities. Unfortuately, the price of polymeric materials is still a significant criterion for individual film layer choice [25, 26].

As it has been mentioned earlier, suitable solutions are the films *containing multiple layers of different types of polymers*, in which the individual layers provide desired properties, in particular the barrier ones [27, 28].



Structure of multilayer films

A - main layer, carrier layer
B - out or top layer
C - barrier layer
D - main layer, color layer
E - layer of recycled material
Hv - Tie layer (glue)

Fig. 1. Structures of Multilayer Films [Weldability of Barrier Films. BP, TBU 2007].

2.4 Multifunctional films

Films made from several polymer types are considered as multifunctional. The examples could be blown films, such as polyethylene. Biaxially oriented polyethylene phthalate films are mostly used in the packaging industry, electrotechnics and as separation films. Multifunctional rolled foils are produced either as polymeric or monomeric. Thin films could be made of polyethylene or polyvinyl chloride by rolling. Special foils are referred to as reflective, protective and ironing foils. Most of these films could be produced in two types, plot or print, and can be laminated as well.

In the packaging industry, usage of laminated materials has been increas. Films provide required barrier and mechanical properties. That is why flooring and waterproofing films can also be included among laminated foil products [10, 29].

2.5 Waterproofing films

PVC films are mainly used as roof or foundation insulation to protect buildings from water, radon and other liquids. It is also employed in the construction of swimming pools, dams or other water structures requiring waterproofing protection.

PVC waterproofing foils are either homogeneous (unvarnished) applied especially as the roof insulation or heterogeneous (reinforced - sandwiched), where a layer of reinforcement is found between PVC, such as a non-woven fabric, textile grid or glass-fiber insert. Their purpose is to increase strength and dimensional stability [30].

Important properties of PVC waterproofing films include high tensile strength, good elasticity and ductility at low temperatures, dimensional stability, weldability and a long service life [31].

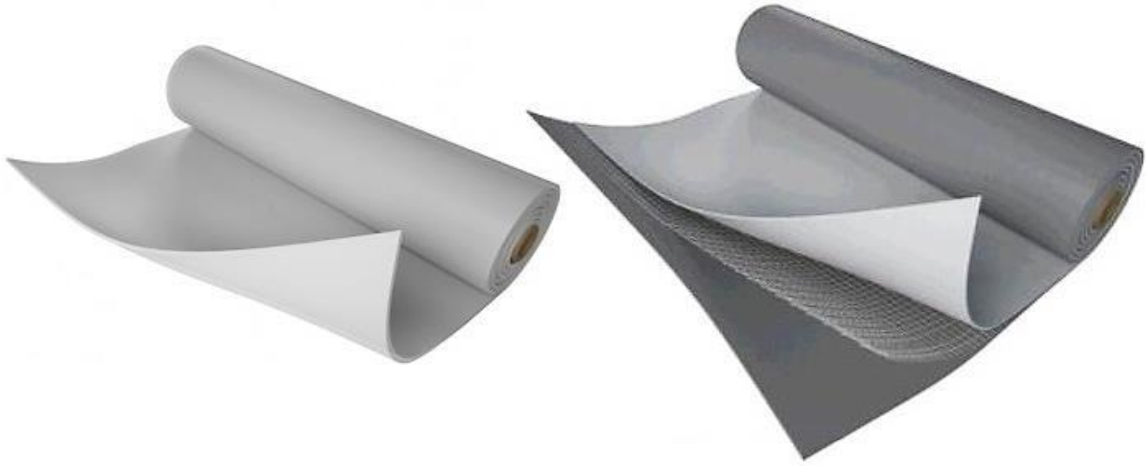


Fig. 2. Waterproofing PVC films – homogeneous (left), heterogeneous with PES grille (right) *[Fatra Napajedla]*.

2.5.1 Recycled PVB films

Thousands tons of PVB films are annually produced to manufacture laminated safety glasses (LSG) for the automotive industry. Such an enormous PVB film production generates waste that might be divided into three groups:

- waste from the film production known as a non-compliant material;
- LSG production waste, trimming = *trim*;
- recycled LSG waste.

The largest share of PVB waste belongs to the category of waste from VBS production. Possibility of using trimmings or automotive glass waste is another step for the future research [32].

Trim

PVB film is highly elastic and shrink-proof, showing good adhesion. Thus, PVB films are also larger than real glass surface in safety glass production. If a film is cut exactly on the edge of glass before adjusting the film to glass, the final film edges show visible imperfections in a subsequent heat treatment.

Sheet cuts of laminated pre-laminated glasses range from 1 to 20 cm depending on the type and geometry of laminated glass and shape of prepared PVB film. Within the current production technology, the amount of trimmings generated in automotive glasses is between 7 to 10% of the total amount of processed film. The amount of pure trim to be recycled depends on the number of new and recycled LSG produced. As the annual production of cars in Europe is 15 millions, recycling capacity reaches from 1.5 to 2 thousand tons [33].

Two methods of separating glass from PVB to recycle glass from VBS may be used:

- dry method,
- wet method.

Dry method

Principle of dry separation is mechanical wiping of the glass from the film. Currently in the Czech Republic, Sklopan Teplice deals with this separation, but the first company that started to employ this technology was ZIPPE Industrielanlage. Pure glass is obtained within this type of separation.

Recycled PVB films contain glass residues, from 0.5 to 4%, depending on the pulp size. However, purity requirements for PVB films are higher for the residual glass, only around 0.02%. This purity is fulfilled only by trim and recycling wet method.

Wet method

A wet process of separation provides a more acceptable solution to separate PVBs from glass with maintaing a relatively good quality of both materials. This method offers more effective removal of glass shards. Basic aqueous solution together with increasing temperature causes the interference of hydrogen bonds. These bonds are responsible for the size of adhesive bonds between residual hydroxyl groups on polymer chain and polar glass.

An acceptable option for using recycled PVB films is their combination with PVC of similar properties. Plasticized PVC is most commonly used in the production of floor coverings or waterproofing foils. This suggests that it would be possible to used recycled PVB to reduce costs and amounts of landfilled PVB [19, 56].

2.6 Nanofillers

As it has been mentioned above, fillers used in manufacturing nanocomposites have at least one dimension in a nanometer size. If only one dimension is in nanometers, then it is a particle in the form of sheets or wafers. If two dimensions are in nanometers, it is the structure of nanotubes. And in case of three nanometric dimensions, isodimensional particles are concerned [34].

Clay minerals are mixed natural materials, composed of finely grained minerals. If they contain adequate amount of water, they are plastic. They harden after firing and drying. Clays mostly contain phyllosilicates, which are silicates with a layered structure. Clays may also incorporate other minerals or organic matter, which may not necessarily affect their properties [35]. Clay minerals are divided into two basic groups:

Clay minerals - together with phyllosilicates, there are also minerals of allophane group, hydroxides, oxo-hydroxides and oxides providing clays with plasticity and harden them after drying and firing. Unlike phyllosilicates, these minerals represent only a small part of clays.

Accompanying minerals – form a part of clay but do not belong to the above mentioned group of clay minerals [36, 37, 39].

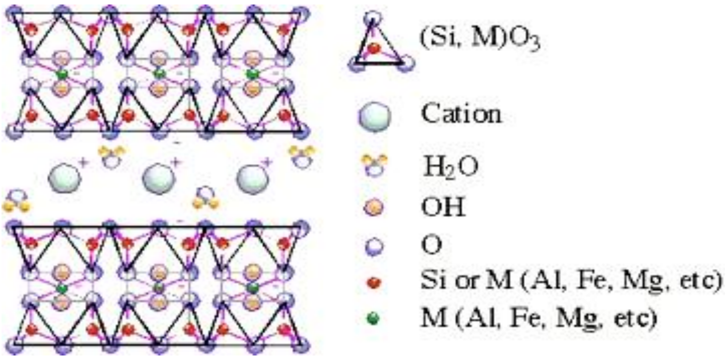


Fig. 3. Basic structure of clay minerals [37].

2.6.1 Montmorillonite (MMT)

Montmorillonite is one of the most important minerals of diocadedric smectite class, silicate class and phyllosilicate subclass. Montmorillonite is typical with tetrahedral positions with almost no or very insignificant degree of Al substitution for Si. Chemical formula of montmorillonite is $(Na,Ca)0,3(Al,Mg)2Si4O10(OH)2\cdot n(H_2O)$ [40].

MMT could be white, gray or pink with yellow or green shades. MMT crystals are built from compact or lamellar substances. MMT hardness is between 1 and 2, its density is 2.35 g / cm^3. If MMT crystals are mixed with water, they can significantly increase their original volume [41, 42].

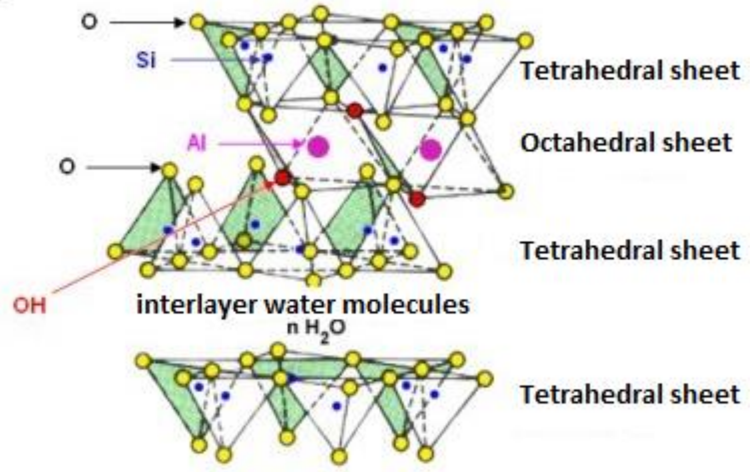


Fig. 4. Montmorillonite structure [38].

Montmorillonite modification

Clay modification enables properties customization for required applications. In the case of this study, MMT was intercalated with organic molecules in a process known as *organophillization* [43].

Organophillization is a process of blending MMT with organic substance which iniciates an intercalation of the compound between the layers and thus increases the distance d between the individual networks. The initial distance *d* between the plates is 9-12Å. Two main ways of intercalation are distinguished [44, 45].

Ion-exchange method

Ion-exchange method is based on the ability of MMT to absorb certain cations and to retain them in an exchange state. The ion-exchange reaction is affected by the action of other cations in the aqueous solution. That is why, it is often referred to as a "wet" path. As salt is formed during the reaction, the final product must be washed [46, 47].

Ion-dipole interaction

Since the early 1990s, Nanocor has been developing a procedure using ion-dipole intercalation. This mechanism is based on the interaction of dipoles of given organic compounds and the interlayer cation. Ion-dipole intercalation is usually performed in the melt of intercalating agent (the phase of washing the by-product is eliminated). Therefore, ion-dipole intercalation is often referred to as a "dry" path [48, 49].

Organic compounds that serve as intercalation agents are mostly substances containing amine-groups (alkylamines) [50].

2.7 Compounding

Compounding is the most important step in the preparation of polymeric nanocomposites. As it has already been mentioned, it is the incorporation of modified nanofiller into polymer matrix in polymer melt. In order to achieve desired properties, both the composition parameters and chronology of individual steps in the process must be respected [3, 51]. Compounding should provide nanocomposite polymer system where nanoparticles will be perfectly dispersed and homogenized in polymer matrix. During compounding, none of the system components must be degraded. As can be seen in Fig. 5, specific terms are used to label the level of perfection of nanofiller mixing - intercalation, delamination and exfoliation of nanofibers in polymer matrix [52, 53].

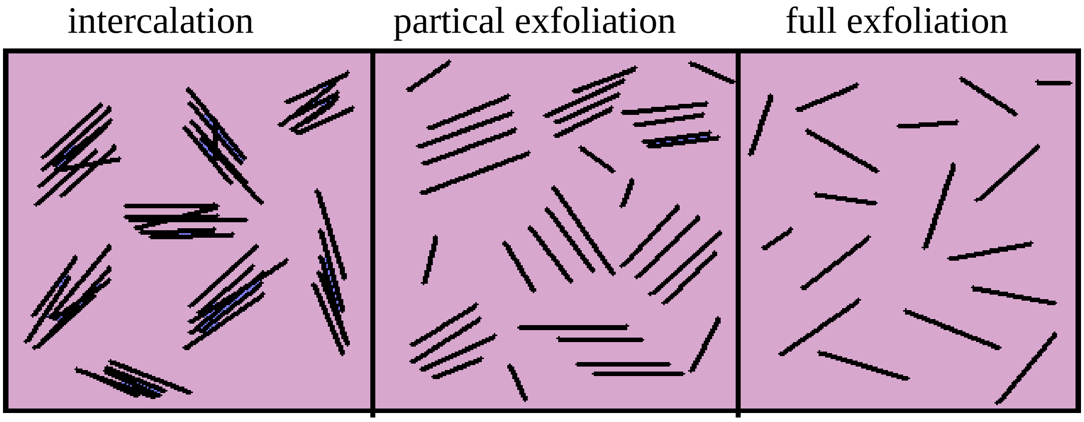


Fig. 5. Degrees of exfoliation of nanofillers in polymer matrix [38].

Requirements for a high level of nanofiller exfoliation in polymeric matrix may be fulfilled in the preparation of nanocomposites based on polar polymers, such as polyurethane, polyamide or polyester. What is more, PVC and nanofiller compounding lead to enhancing of nanocomposite properties [54-56].

Due to hydrophobic nature of polyethylene and polypropylene chains, compounding is more complicated than in the previous cases. In addition to nanofiller modification, compatibilizers, such as PP or PE enhancing affinity to the surface of clay montmorillonite, are added to these types of polymers. PP and PE compatibilizers are fundamentally the same polymers modified by chain-linked polar substituents. These substituents could be styrenes, methyl methacrylates, hydroxyl groups or most often maleic anhydride. Content of polar groups and compatibilizer concentrations in the mixture may vary. Exfoliation of nanofibers in polymeric matrix is improved with an increasing polarity of the mixture. However, at the same time properties of such polymer matrix may be deteriorated due to a change in the system layout [57, 58]. Regularly, up to 5 wt. % of compatibilizer is added. Considering EVA nanocomposites preparation, compatibilizer is not applied due to a higher polarity of polymer matrix affected by the content of vinyl acetate groups [59, 60].

Level of exfoliation depends on the influence of chemical or structural properties and also on the used composing device. During the process of compounding, there is an effort to provide the system with the energy or forces to disintegrate montmorillonite monocots to individual plates and to disperse them homogeneously in polymer matrix.

Complete, perfect exfoliation of nanofiller in polymer matrix is the key factor in the preparation of nanocomposites with desired properties. Within further research of nanocomposites it has been found that nanomaterials may significantly influence also other properties, such as thermal stability, degradation and gas permeability. As an example may serve a case of reduced permeability for gases. It is assumed that oriented exfoliated nanoparticles prolong the distance of the gas passage through films [61, 62].

3 TECHNOLOGY OF FILM PRODUCTION

Extrusion, blowing and rolling are the most common methods of film production. Extrusion is a manufacturing process in which plastic melt is continuously extruded through a profiling device (extrusion head) into free space. Extrusion technology is used to produce finished and semi-finished products, foil or board. This production process employs a screw extruder as a part of production lines. In this study, EOC samples were extruded.

Blown film production technology is based on the process that a parison with a wall thickness of from 0.5 to 2 mm is still in its plastic state inflated by compressed air (magnification from 2 to 5 times) and at the same time stretched by a pulling device (up to 5 times longitudinal stretching). Blown film of a wall thickness from 0.015 to 0.3 mm is then cooled and wound.

Blow molding produces LDPE, HDPE and PP, PVC, PA and PETP films, multi-layer films of different material compositions. Today, seven or twelve-layer films may be produced using this method [63, 64].

Most often, foil top version is applied for blowing multilayer foils. Extruder is fitted with a blow head. Extruded foil with a predetermined overpressure (0.15 to 1 kPa) is blown and cooled by air which is fed through the cooling ring and uniformly blows the film over the entire circumference. Obtaining uniform thickness is conditioned by cooling. The air is fed to the foil sleeve through the extrusion head and the blown sleeve is gradually cooled and eventually flattened between the folding plates. Afterwards, the line closes the pull-out and winding device. Extraction speed may be controlled and so influences thickness and longitudinal orientation of the film. The film can be trimmed either on one or both sides. PE, PP, EVA and SRL samples were blown in this study [16, 65, 66].

Rolling is a method of continual shaping of plastic material in a plastic state in a slot created by a pair of rollers rotating against each other. The passage of the molded mass is uniformed. The feed material is compressed, accelerated, retracted and released between the rollers. The course of these changes is influenced by the type and state of molded material fed into the slot, by the peripheral speed of the rollers and slip value, temperature of cylinders and other qualities. Rolled-up materials are malleable and adhesive. They could be easily removed from the rolls. Softened PVC is a typical example of a plastic manufactured by rolling. To produce softened PVC foils, type of material is selected primarily according to the requirements of the final PVC mixture properties [25, 67, 68].

4 EXPERIMENTAL PART

CHARACTERIZATION OF FILMS PROPERTIES

4.1 Sample preparation

Polymer matrix of PP, PE, EVA and Surlyn samples containing nanoparticles were mixed on Scientific LTE 20-40 twin-screw extruder and subsequently granulated. Extrusion head temperature was set to 210 °C for PP, 160 °C for PE and EVA and 200 °C for Surlyn, the speed was 150 minutes per minute. Extruded string was cooled in a water bath and then granulated.

Samples with LDPE and EOC were prepared using the same process. PVC and PVB samples were prepared in two steps. Firstly, PVC and PVB mixture was stirred on a two-screw extruder BUSS with the head temperature of 160 °C (in co-operation with Fatra, a.s.). Resulting string was granulated and the granules were mixed with nanofibers using a kneader of FT UTB in Zlín at the temperature of 150°C. Finally, plates of 125 x 125 x 2 mm were molded.

4.2 Sample evaluation

Mechanical properties

Mechanical properties were measured on Galbadini Quasar 25. Two-sided vane shaped specimens were tested respecting EN ISO 527-3 (64 0604) at two tearing rates - the initial velocity was 1 mm / min in 2% module. Then the speed was increased to 100 mm / min until causing a fracture.

Dynamic mechanical analysis (DMA)

DMA measurements were performed on 20x5x2 mm samples from pre-shaped DMA Perkin Elmer plates. E module and tan δ (tan delta = E "/ E ') were determined ranging from 1 to 200 Hz in a 2 Hz step and at the temperatures between -100 °C and + 100 °C.

Barrier properties (GTR, OTR)

Barrier properties were established using Julabo TW8 and CSN 64 0115 standard volume method. Test bodies were in the shape of a circle with a diameter of 80 mm. Pressure was set to 2 bars and temperature to 35 °C. N2, O2 and CO2 were measured and obtained values were subsequently recalculated according to ASTM D 3985-05.

Transmission electron microscopy (TEM)

Ultra-thin sections were prepared using Leica Ultra-Cryo-Microtome at -100 °C. Transmission electron microscopy was performed on JEM 200 CX at the accelerated voltage of 100 kV.

Differential scanning calorimetry (DSC)

DSC test was performed on Mettler Toledo DSC 1 with an external cooling unit. The rate of cooling and heating varied in particular cases (5, 10, 15 and 20 °C per minute) and the temperature ranged from -90 °C to 140 °C.

X-ray diffraction analysis (XRD)

X-ray diffraction analysis was performed using URD diffractometer in the laboratories of FT UTB. This method was chosen to determine the intercalation or exfoliation of the filler in the blends. Measurements were performed at the voltage of 40 kV and current of 30 mA. The area observed to prove the presence of clay fillers was from 2 ° to 8 ° 2 θ.

Accelerated degradation

Accelerated aging test was performed in Xenotest Alpha. UV radiation was applied with reference to the conditions defined in EN ISO 4892. Temperature was 38 °C, filters simulating daylight emitted 60 Wh / m and 50% RH was set. One measurement cycle lasted for 46 days and simulated one-year degradation.

Fourier transmission spectroscopy (FTIR)

FTIR test was performed on some samples (those after accelerated aging test) using FTIR spectrometer AVATAR 320 (Nicolet) with wavelengths between 4000 and 500 cm^{-1}. Spectral change between 1810 cm^{-1} and 1681 cm^{-1} was observed due to material degradation during the irradiation.

Hardness

Hardness test was performed using Shore A hardness tester respecting the Czech national standard ČSN EN ISO 868. Measurements were realized under the standard conditions at laboratory temperature of 20 °C using film remainders of 50x20x2 mm. A test body, thick in total 6 mm, consisted of three two-millimeter foils placed on top of each other. Determination was based on pressing the hardness tip into softened material. Instantaneous hardness values (1 s after a contact between the support foot and the test body) were recorded. Five measurements were performed at different locations of each test body.

5 SHORT EVALUATION OF STUDIED POLYMER FILMS

5.1 Characterization of films with nanofillers

Initially, test films were prepared from polypropylene, polyethylene, EVA and Surlyn (SRL). Based on measured mechanical and barrier properties, polyethylene, specifically LDPE, was selected for further testing and preparation of nanocomposite suitable as a part of multilayer polymeric film.

5.1.1 PP, PE, EVA and Surlyn films

The study of nanocomposites focused on polymer films preparation from polyethylene (PE), polypropylene (PP), surlyn (SRL), ethylene vinyl acetate (EVA) and different types of MMT. Due to various polymers and clay application, maleinized types of these materials had to be added to enhance miscibility. Foils were blown on a laboratory blower. Results were compared with pure foils; barrier properties, morphology and mechanical properties were evaluated. Results showed that the use of nanoparticles at 5% concentration in ethylene copolymers (Surlyn and EVA) appears to be a suitable option for further testing.

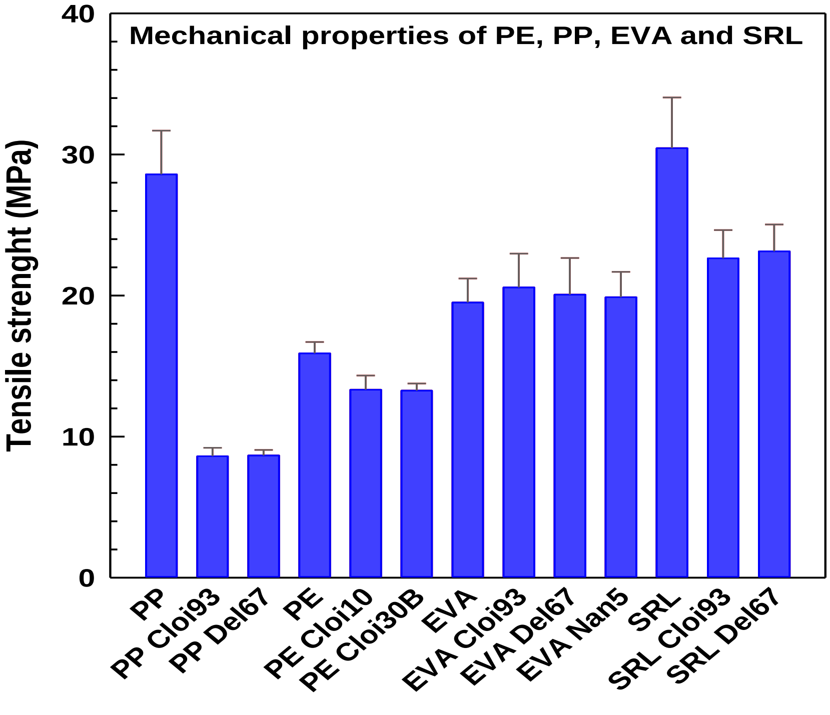


Fig. 6. Mechanical properties of nanocomposites

As can be seen in Fig. 6, the values of pure PP, PE and Surlyn materials are higher than the values of the same materials enriched with fillers. Particularly for PP, added nanofillers significantly reduced tensile strength. The only exception may be materials containing EVA with the values slightly higher for filled samples. Concerning elongation at break, the largest percentage of elongation was obtained at materials filled with EVA. EVA samples with 5% Cloisite 93A nanofiller showed the best traction elongation properties. Fillers content in PP did not significantly deteriorate ductility. Tensile modulus reached higher values for the samples filled with PE and Surlyn. Within the samples with EVA, the increase of the modulus was rather insignificant.

In addition to mechanical properties, barrier properties of these films were measured. XRD and TEM analyses were performed and water vapor permeability was tested.

Based on obtained results, LDPE was determined as a representative of polyethylenes. It is widely used in the production of blown multilayer films.

Optimal conditions for the preparation of blending with nanofiller were established and subsequently, two representatives of nanofillers were selected for further testing and modifications - Cloisite 93A and Dellite 67.

After the initial testing of the selected polymers, a representative of commercially commonly used materials, low density polyethylene, was chosen. In accordance with literature and past experience, LDPE is one of the most widely applied materials in the production of multilayer films. It may also be filled with nanofibres to enhance some of the material properties.

Apart from commonly used polyolefins in the packaging insustry, such polyethylene and polypropylene, there occurred an opportunity to test mixing these nanofillers into non-traditional polymers, such as EOC. EOC is a new polyolefin elastomer, developed by Dow Chemical Company (Delaware, USA) employing metallocene catalysts. As it has valuable properties, it attracts growing attention of both the research and industry. The presence of octene in EOC comonomer affects the level of crystallinity and provides greater flexibility of copolymer. EOC may be considered as elastomeric polymer. Typically, octene content in copolymer is between 17 and 45 wt. % [8 - 12].

5.1.2 EOC films

The copolymer of ethylene, namely ethylene-octene (EOC), was been chosen for further study of nanofibers use in polymer films. Two different types of EOC (EOC-17 and EOC-45, depending on the content of octene groups) and one type of MMT - Cloisite 93 (in three different concentrations of 3, 5 and 7 wt. %) were studied. Increase in EOC tolerance to nanoparticles was achieved by the addition of maleinated PE (5 wt. %). Material was homogenized on a twin-screw extruder and the foils were extruded through a wide slot head. Such polymeric films were tested for their barrier and mechanical properties, morphology and degradation of nanocomposites. Results of barrier properties of ethylene-octene copolymers proved significantly better properties of EOC-17 (17% of octene groups in copolymer) for all gases. This fact may be due to a lower octane content and higher crystallinity. It could be concluded that Cloisite 93 nanoparticles may improve barrier properties of EOC polymer matrix. Because after applying nanoil (ideally 5 wt. %) into EOC matrix, gas permeability decreased.

Ethylene-octene copolymer may be used in the packaging industry, either alone or in the combination with PE or PP. Therefore, its barrier properties for N_2, O_2 and CO_2 were measured.

Gas permeability results for EOC-17 and EOC-45 copolymer / nanocomposite clay can be seen in Fig. 7. Compared with pure materials, filled EOC systems show lower throughput for all monitored gases. The best combination seems to be filling by 5 wt. % Cloisite 93, which is also confirmed by the results of mechanical properties and TEM.

If these two ethylene-octene copolymers are compared, EOC-17 exhibits significantly better properties for all gases. This may be due to fewer octane groups and higher crystallinity.

It may be concluded that Cloisite 93 nanoparticles enhances barrier properties of EOC polymer matrix. Gas permeability decreases after nanotube application in EOC matrix, with ideally 5 wt. %.

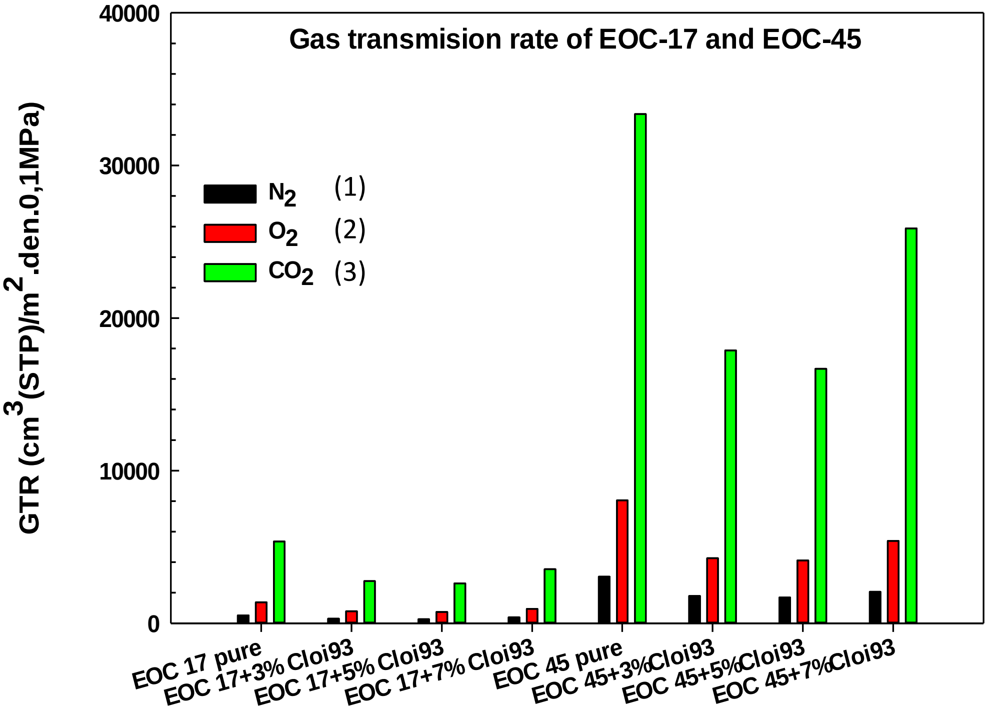


Fig. 7. Barrier properties of EOC samples - N_2, O_2 and CO_2.
(1) first column

This effect may be initiated by better distribution and dispersion of nanofiller in polymer matrix and by better exfoliation of MMT nanoparticles in polymer matrix. However, it has been known that the ideal orientation of MMT plates in polymer matrix during the samples molding is impossible to achieve.

Molded samples, films, are pressed into very thin plates. Thickness of the molded film is about 50 µm and the size of MMT plates is in nanometers. That is why, the orientation of MMT plates in polymer matrix cannot be excluded.

Comparison of the nanofibers distribution in EOC-45 matrix with variable clay contents can be seen in Fig. 8. Distribution is approximately the same in both cases. However, as the figures show, if EOC-45 contains 5 and 7 wt. % of nanoparticles in polymer matrix, exfoliation is worse.

It is evident that the concentration of 5 wt. % of nanofibers in polymer matrix leads to more significant exfoliation of filler nanoparticles in polymer. While at the concentration of 7 wt. %, nanoparticles may form agglomerates and filler exfoliation is imperfect.

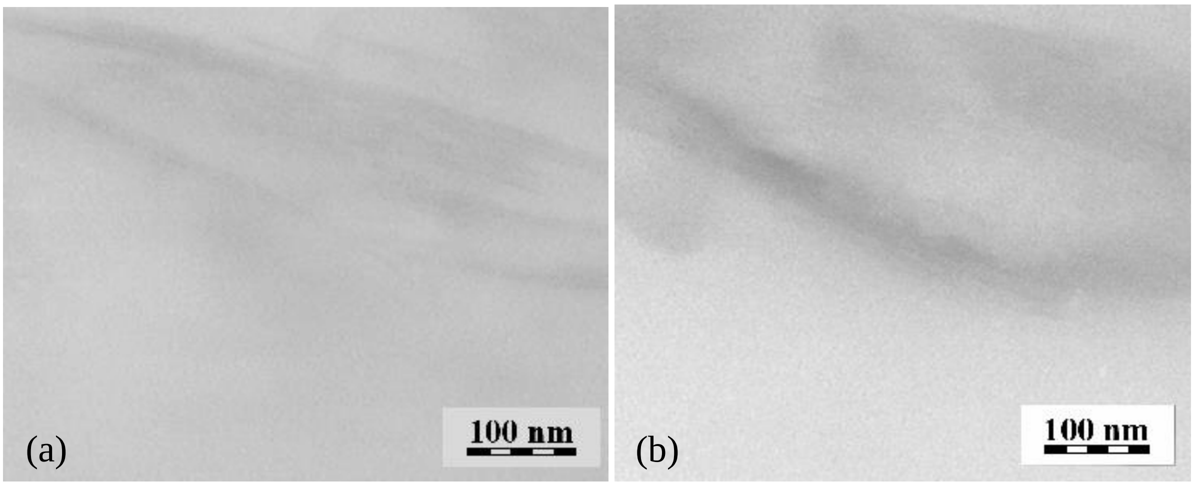


Fig. 8. TEM pictures: (a) EOC-45 (Engage 8842) with 5 wt. % Cloisite 93, (b) EOC-45 (Engage 8842) with 7 wt. % Cloisite 93.

Next study of polymer films applying results of the previous research of EOC copolymers was based on another type of MMT (Dellite 67). The influence of nanoparticles on octene group content in EOC was determined. Based on previous measurements, 5% concentration of nanoparticles in polymeric EOC matrices was chosen. Samples were homogenized on a twin-screw extruder and subsequently extruded through a wide-slotted head. Degree of exfoliation (intercalation) of nanofiller in polymer matrix, barrier and mechanical properties and degradation of the films due to the UV radiation were tested and compared with previous studies. Distributions of nanofibers in EOC-17 and EOC-45 matrix with 5% clay content were compared. TEM analysis results suggested that EOC blending with nanoparticles was successful. Although distribution of nanoparticles in EOC-17 matrix was comparable, exfoliation was slightly better in EOC 17 with 5 wt. % Dellite 67 in polymer matrix. TEM results confirmed XRD conclusions, which proved significantly improved exfoliation of nanocomposite in EOC-45. In general, the best results were achieved with MMT exfoliation in EOC-45 with 5% Dellite 67.

5.1.3 PVC/PVB films

In addition to the use of nanoparticles in polymer matrix, further possibilities to prepare films from recycled PVB was investigated. The basis of polymer matrix was formed by PVC with different PVB content (pure and recycled) from 0 to 100%. Films were rolled on a two-roll laboratory machine and samples were subsequently pressed to maintain the same thickness. Possibility of applying recycled PVB from automotive glass as a substitution for PVC was examined. Appropriate PVB concentration in PVC matrix was assessed mainly based on the evaluation of mechanical properties, hardness and reflective elasticity. Filling of 80% of PVBs, both recycled and non-recycled, appeared to be optimal (considering mechanical properties). These results confirmed previous measurements of PVC / PVB mixtures with mechanical properties deterioration from 10% to 50% of PVB values and enhancing again from 60% to 90%.

Table 1. Mechanical properties of PVC/PVB blends and PVC/recycled PVB blends.

	PVC/PVB		**PVC/rec.PVB**	
Composition PVC/PVB	**Tensile strength (MPa)**	**Elongation (%)**	**Tensile strength (MPa)**	**Elongation (%)**
100% PVC	15,78	352,82	15,78	352,82
10 % PVB	11,87	242,26	12,54	240,79
20 % PVB	10,44	192,48	10,62	186,63
30 % PVB	10,09	185,68	10,75	185,61
40 % PVB	12,43	183,10	11,13	181,06
50 % PVB	13,62	210,64	13,92	201,42
60% PVB	15,96	227,62	15,41	216,35
70% PVB	17,27	231,12	17,29	217,17
80% PVB	**18,57**	**236,92**	**18,83**	**221,50**
90% PVB	17,89	228,38	17,21	199,41
1000% PVB	18,37	218,22	17,84	178,65

Table 1 compare the results of mechanical properties for PVC / PVB and recycled PVC / PVB systems. According to mechanical properties, 80% PVB filling seems to be the optimal ratio for both systems. These results have confirmed the previous measurements of PVC / PVB mixtures with decreasing mechanical properties in the range from 10% to 50% and increasing from 60% to 90% again.

From the mechanical properties point of view, PVC / PVB ratio of 20:80 is optimal. However, mechanical properties may not be the only criterion. Therefore, further properties, such as hardness, dimensional stability, thermal and light degradation were measured as well.

DSC analysis was conducted to define polymer miscibility. Glass transition temperatures (T_g) of pure (non-blended) plasticized PVC and PVB were established. T_g of plasticized PVC was -29.5 °C and T_g of PVB 16.8 °C.

Obtained curves are shown in Fig. 8. Furher experiments focused on T_g values of selected blends. Polymer immiscibility was determined by two glass transition points, at a ratio of 20% and 80% of PVB. The glass transitions at temperatures of -40.6 °C (PVC part) and 28.2 °C (PVB part) were determined in a blend containing 20% of pure PVB and -29.6 °C (PVC part) and 18.1 °C (PVB part) in a blend consisting of 80% of pure PVB.

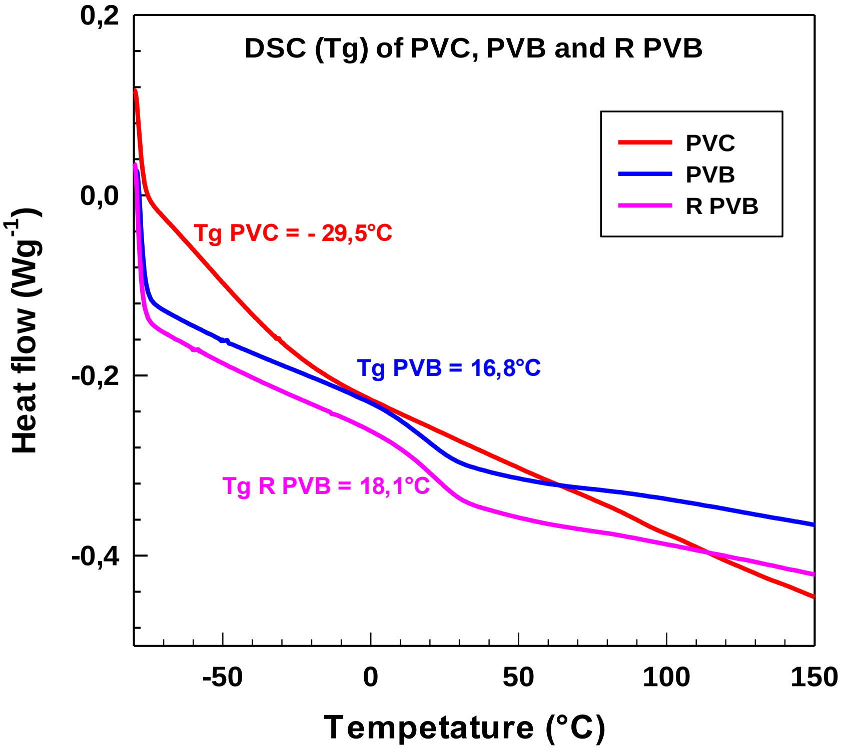


Fig. 9. Glass transition temperatures of pure PVC, PVB and recycled (R) PVB polymers determined by DSC analysis.

This study clarifies suitability of recycled PVB application in the industry, especially in PVC blends. Not only may recycled PVB be acquired at acceptable cost, unlike PVB, it also performs decent mechanical properties and is not degraded during its lifetime.

CONCLUSION

Results in this paper are mainly focused on the possibility of using nanoparticles, especially MMT, as a part of polymer films. Selected types of MMT and polymers, possibility of successful mixing at different concentrations and the evaluation of basic physical and mechanical properties were observed. In addition to nanofibers use in various polymeric matrices, possibilities of films production from waste materials, especially PVB, have been investigated.

Comparison of mechanical and barrier properties and exfoliation of the nanofiller in the polymer matrix was studied. If the montmorillonite platelets are not dispersed and stay in origin agglomerates, it may cause deterioration in the desired properties. The goal of the production of polymer nanocomposites is to achieve the full exfoliation. Good exfoliation of fillers can improve mechanical and barrier properties of nanocomposites. Results of the mechanical properties measurement show that the nanofillers in matrix provided different values in comparison with the polyolefins matrix. The observation that nanofillers within the polymer matrix affect polymer properties is important. The results of gas permeability may be influenced by varying the thickness of the films. It can be said that efficient exfoliation of fillers can improve mechanical properties of nanocomposites. Nevertheless, the degree of exfoliation and orientation of the platelets is the most crutial parameter.

CONTRIBUTION TO SCIENCE AND PRACTICE

The most important contributions of the doctoral thesis to science and practice can be summarized as follows:

- Better understanding of the preparation of polymer films, multilayer films, nanocomposites with clay nanofillers; developing of an optimalized technologic prossesing.
    - *Outputs gathered within this part of the thesis can be used under preparation of polymeric, special and multifunctional films.*

- The formulation of using of recycled PVB in multifunctional films.
    - *This part of the work notably contributed to description of recycled PVB which are suitable to using in polymer multifunctional films.*
    - *The output: Utility model - Polyvinyl butyral recyclate for the preparation of polymer blends and polymer mixtures containing it - from 15. 9. 2016.*

Other results described in the chapter "Contribution to Science and Practice" have not been mentioned in the doctoral thesis because they do not corespond fully with a set of published articles. However, they are consistent with the topic and objectives of the doctoral thesis and they also create the next part of my doctoral studies and research.

- The successful preparation of multilayer polymer film with better possibility of recycling.
    - *The mixture for pre- production of multilayer PE film was also prepared. Based on previous measurements, testing and production requirements, polyethylene LDPE LD 100 AC, Modified Cloisite 93A clay in 5 wt. % concentration (modified in Synpo Pardubice) and Priex 15005 as compatibilizer were selected for pre- production. A five-layer blown film with a thickness of 0.070 mm (70 µm) from the prepared mixture was made in Invos Svárov.*

- The development of novel special antibacterial films.
    - *Nano Ag and nano Fe in polymer matrix and encapsulated essential oils on the surface of the foil were prepared and evaluated (cooperation with UPOL Olomouc, Synpo Pardubice and Invos Svárov)*
    - *The output: Utility model - Multilayer packaging film with antimicrobial effects and method of their production - from 14. 12. 2015.*

- The formulation of using of recycled waste of waterproofing films in special aplications.
    - *The doctoral work also contributed to description of recycling proces of PES waste as a part of waterproofing film which are suitable to using in other polymer special and multifunctional films and in building industry.*
    - *The output: Utility model - Universal pad used in construction - from 24. 7. 2017.*

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LIST OF ABBREVIATIONS

UV	Ultraviolet radiation
PE	Polyethylene
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
PVB	Polyvinyl butyral
EVA, EVAC	Ethylene-vinyl acetate
SRL	Surlyn
EMAA	Copolymer ethylene with methacrylic acid
TIE	Adhesive layer
g/m^2	Gram per square meter
g	Gram
m^2	Square meter
LDPE	Low density polyethylene
g/cm^3	Gram per cubic centimeter
cm^3	Cubic centimeter
O_2	Oxygen
N_2	Nitrogen
CO_2	Carbon dioxide
EOC	Ethylene-octene copolymer
Na^+	Sodium Cation
MPa	Megapascal
Pa	Pascal
cm	Centimeter
m	Meter
mm	Millimeter
NC	Nanocomposite
MMT	Montmorillonit
ČSN EN ISO	Czech national standard
ASTM	American technical standard
TEM	Transmission electron microscopy
XRD	X-ray diffraction analysis
DMA	Dynamic mechanical analysis
cm^{-1}	Reciprocal centimeter

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TAČR - TA03010799 (1/2012-1122015)
Usage of nanomaterials and natural extracts as funtional substances in the development of active packing materials with barrier, antimicrobiotic, protective and oxygen absorbing effect
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TAČR - TH 01030054 (1/2015-12/2017)
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