

Barrier Properties of PE, PP and EVA (Nano)composites – the Influence of Filler Type and Concentration

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Abstract: - Nanocomposite materials with layered clay used as nanofiller and polyethylene (PE), polypropylene (PP) and copolymer ethylene and vinyl acetate matrix (EVA, the content of VA component 19 wt. %) were prepared by compounding the individual components in Brabender kneader. The MMT Na⁺ and four types of commercial products such as Nanofil N 5 and N3000, Cloisite 93A and 30B were used as nanofillers. Next to the clays microprecipitated CaHCO₃, nanosilica and Halloysite tubes were used. The quantity of all the above-mentioned (nano)fillers was 1, 3 and 5 wt. % in relation to the content of montmorillonite. The aim was to evaluate the influence of (nano)filler type and concentration on nanocomposite barrier properties.

The morphology of nanocomposite samples was examined by means of XRD analysis illustrated by transmission electronic microscopy TEM. Furthermore, permeability for O₂ and CO₂ were observed.

Keywords: (nano)composites, clay, barrier properties, polyolefins

PASC: 82.35.Np Nanoparticles in polymers

INTRODUCTION

Polyolefins is a group of polymers with a very low polarity character. Due to this fact, the mixing them with organic fillers is very difficult. It is very problematic to achieve a good compatibility of a polymer matrix with filler particle surface and by this to obtain required improvement of properties. This holds true for preparation of polymer nanocomposites¹⁻⁵. Generally, polyolefins are not willing to form intercalated or even exfoliated nanocomposites in the presence of a layered silicate clay as smoothly as polar polymers such as poly(amide)s^{5,6}. This problem can be solved or by using “compatibilizers” (maleated PP or PE) or by polar side-chains grafted to the polyolefin backbone have been utilized to aid in the intercalation and exfoliation of layered clays^{7,8}. Nowadays also EVA polymer is used - the number of works based on the study of EVA copolymer and even EVA nanocomposites has become wider and wider¹⁰⁻¹². Nanofiller combined with PE, PP or EVA copolymer matrix not only improve the gas barrier properties, but also increase a wide range of other useful properties, such as tensile strength and modulus, flammability resistance etc¹³⁻¹⁵. Another big advantage is the possibility of easier recycling in comparison with the common types of fillers.

Nanocomposites, as it is well known, are prepared by mixing polymer matrix with nanofiller. Generally, they represent layered silicate minerals - clays, where the thickness of the individual leaves is in nanometer size. The most frequently used type of nanoclay is montmorillonite (MMT)¹⁶⁻¹⁹. It is a layered mineral belonging to a group of clay minerals with octahedral and tetrahedral nets in the ratio of 2:1. In order to increase its exfoliation in the polymeric matrix, it is modified by the process known as organophilization or intercalation, i.e. the insertion of a suitable organic compound into MMT interlayer²⁰⁻²⁴. This way, a broader d-spacing as well as reduction of gravitational forces between the individual platelets of montmorillonite are reached. Consequently, this leads to the reduction of energy needed for the breakup of nanofiller into the individual nanoleaves in the polymeric matrix after the process of compounding²⁵. The function of MMT nanoleaves in the polymer matrix can be observed from two points of view. Generally, the first one is the original effect of filler - the improvement of mechanical properties by increasing the filler surface. The effect of nanofillers rests on the ability to create this effect by much lower loading in comparison with common fillers. Another quality of nanoleaves is their positive impact on the orientation of long thick platelets in polymer matrix after compounding, where they are arranged in such a way that they create a gas barrier to the gas transmission. So, the gas permeability is lower. The principle of this phenomenon is shown in the Figure 1.

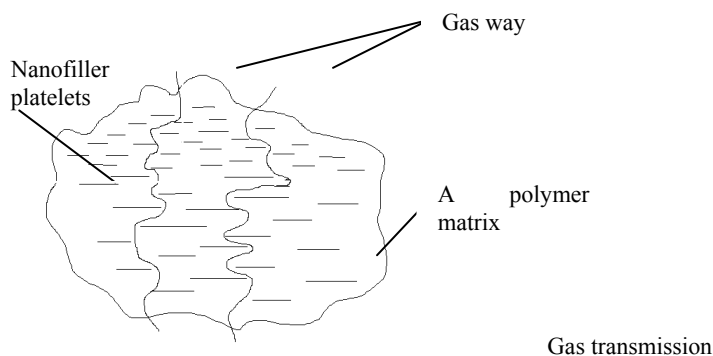


FIG. 1. The principle of gas transmission on polymer nanocomposite matrix

This article was focused on the preparation of PE, PP and EVA copolymer clay nanocomposites with two different montmorillonite concentrations in order to evaluate the influence of various type and loading on prepared nanocomposite properties, such as morphology, mechanical properties and gas barrier properties.

EXPERIMENTAL

Nanofillers

Cloisite[®]Na⁺ (nonraterated MMT), Nanofiller N5 and N3000 Nanofils from Sudchemie Germany and Cloisites 93A and 30B from Southern Clay Chemistry, microprecipitated CaHCO₃, nanosilica and Halloysite tubes were used for filling all matrices. The quantity of all the above-mentioned nanofillers added to the polymeric matrix was 1, 3 and 5 wt. % in relation to the content of MMT.

Polyethylene DOWLEX 2035 E was supplied by company Dow Chemical Company. Maleated polyethylene was produced by Dow Chemical Company too.

Polypropylene Mosten from Chemopetrol Litvinov, Czech Republic, maleated PP (PPMa) EXXELOR PO .

Copolymer matrix used: EVA copolymer – GREENFLEX FF 55 (VA content 19 wt. %, melt index 0.7, density 0.92 g/m³), from Polimery Europa.

Mixture blending

PE and EVA mixtures with nanofillers were blended in one-screw extrusive Brabender machine at the temperature of 150; 180 and 220°C, rpm 30 min⁻¹.

The homogenized matter came out cold by the air in the form of a string and was subsequently granulated.

The prepared granular was used for pressing plates. The pressing took place at the temperature of 200 and 230°C.

Film pressing

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

Evaluation of the samples prepared

Gas barrier properties

The observed nanocomposite molded films with the thickness of about 50 μm were used for the measurement of O₂ and CO₂ permeability, the equipment based on ČSN 64 0115, method of a constant volume.

RESULTS AND DISCUSSION

XRD. In order to discover the result of montmorillonite exfoliation in used matrices, XRD patterns have been taken. According to the recorded results was possible to observe that no complete montmorillonite exfoliation has taken place. All plotted patterns show at least one peak which belongs to the MMT. To sum up, the complete exfoliation of nanofiller has not taken place in any clay mixture prepared. Moreover, the result is not influenced by MMT concentration and this holds true for all nanofillers observed.

As discussed below, despite the incomplete exfoliation shown by XRD measurement, a certain improvement of some qualities observed has taken place. The distribution of next types of used (nano)filler was evaluated by TEM and the good level of it was approved.

Permeability. As mentioned above, PE, PP and EVA copolymer are polymers used in packing industry. Therefore, our study also covers the values of permeability for O₂ and CO₂, which are mediums that should be prevented from penetrating through film, e.g. in case of food wrapping.

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

The evaluation of the O₂ permeability (see Fig 2) shows for PE, PP and copolymer EVA matrices. The nanofiller Cloisite 30 B is totally unsuitable, for all used polymers, similar result was achieved for microprecipitated CaHCO₃, nanosilica and Halloysite tubes. Only for nanofillers N 5 and 3000 and Cloisite 93A the result of permeability observation was better in the comparison of unfilled matrices. In Fig. 3 the measurement of CO₂ permeability is presented. The result is the similar like for O₂ observation. Also for CO₂ Cloisite 30B confirmed the position of bad filler for these matrices. Unfortunately, in case of EVA no nanofiller showed the significant lowering of CO₂ permeability. The best lowering for gases permeability was achieved for the combination of PE and Cloisite 93A.

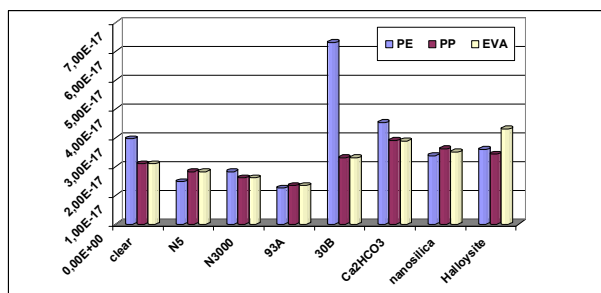


FIG. 2. Graph of O₂ permeability (5%wt filling)

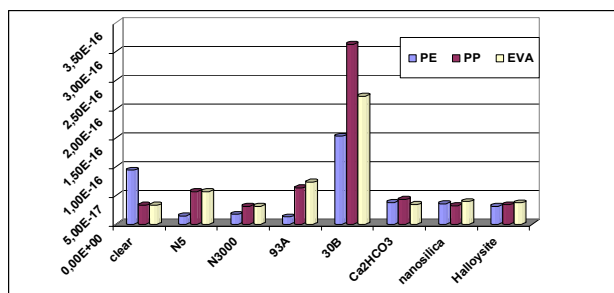


FIG. 3. Graph of CO₂ permeability (5%wt filling)

CONCLUSION

PE, PP and EVA copolymer matrices with seven types of commercial (nano)fillers with the different structures, particles type and size were prepared and observed. Because of using of mentioned materials for food packaging, the morphology of prepared samples, mechanical properties and barrier properties were checked. Although the TEM and XRD measurement did not show the full exfoliation of clay nanofillers in the polymer matrix, the very good result in case of mechanical and barrier properties were found, especially for PE matrix. Cloisite 30B was found not to suitable for these types of polymers. Higher concentration (5%wt) brought more significant lowering of gases permeability.

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