Barrier Properties of Filled High-impact Polystyrene

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Abstract: This work is focused on the evaluation of the effect of different kinds of fillers with various concentrations in high impact polystyrene on barrier properties, hardness and resilience. The aim is doing comparison of the effect of different kinds of fillers and nanofillers on gas and water permeability. Dispersion of nanofiller in polymer matrix was determined by X-ray diffraction and transmission electron microscopy. Gathered results indicate that there is a correlation between the size of the filler particles and final compound properties. Some samples showed an improvement of barrier properties.

Key-Words: High-impact polystyrene, composite, nanocomposite, nanofiller, gas permeability, water permeability.

1 Introduction

Polystyrene is a commodity plastic manufactured on a very large scale. The brittleness of polystyrene considerably limits its use in some applications. The toughness of polystyrene can be improved by copolymerization or blending with a butadiene elastomer or other rubberlike polymer (the rubber should be present as a separate dispersed phase). This polymer is known as the high-impact polystyrene (HIPS) [1]. The most common applications for HIPS are in television and computer cabinets [2], electronic instruments and building materials. [3] HIPS is used in food industry (food boxes and packaging) as well.

Permeability for gas and water vapor is important in this branch, and also in other branches, where it is necessary to reduce or control these values.

In contrast to virgin polymers or to conventional composites, polymer/clay nanocomposites are an important class of emerging materials. They have demonstrated significantly enhanced properties in number of areas [4], e.g. barrier and mechanical.

Polymer nanocomposites are prepared by dispersing a filler material into nanoparticles that form flat platelets. That is why the dispersion has high importance for influence on properties of nanocomposites. The dimensional disparity results in a large aspect ratio which is a property conducive to barrier enhancement based on the principle of tortuous path migration [5,6] in which impermeable nanolayers impede the diffusion of solvent molecules varied in intercalate or exfoliate structure. The exfoliated nanocomposite restricts the diffusion path more in comparison with intercalated or conventionally filled micro composites [7].

This work is focused not only on evaluation barrier and mechanical properties of clay nanocomposites but also on wide variety of other fillers of spherical (micromilled calcite and modified nanosilica) and of long thin tube (organosilicate nanotubes) particle shape.

2 Experimental

2.1 Materials

Commercial high-impact polystyrene KRASTEN® 552M (SYNTHOS Kralupy a.s.) was used as a polymer matrix. The following fillers were used: micromilled calcite Omya EXH 1sp (Calplex), modified silica Aerosil R812 (Degussa), organosilicate nanotubes Halloysite (Sigma-Aldrich) and organically modified layered clay nanofillers Nanofil 5 and Nanofil SE3010 (Südchemie).

2.2 Preparation of samples and speciments

The composite samples were prepared by kneading in laboratory Brabender Plasti-Corder mixing bowls for 10 min. Temperature was 200 °C and the rotational speed 30 min^{-1}.

The specimens for evaluations were prepared by compression molding at the temperature 195 °C for 3 min.

2.3 Instrumentations

X-ray diffraction (XRD) measurements were performed using PANalytical X´Pert PRO diffracto-meter with a Cu tube source (λ = 0.1540 nm) operated at 1.2 kW.

Specimens for the transmission electron microscopy JEM 200CX (TEM) were cut using Leica cryo-ultramicrotome at a sample temperature of -100°C and at a knife temperature of -50°C to obtain ultra-thin sections with the thickness approximately 50 nm and an acceleration voltage of 100 kV was used.

Mechanical properties namely, resilience and hardness Shore D, were done. Resilience was measured on Schob machine according to norm ČSN 62 1480. The weighting of 37.5 N was applied for measurement of hardness according to norm ČSN EN ISO 868, values were read after 15 s.

Water vapor permeability and gas permeability for nitrogen and air were measured as barrier properties. The first one was measured by norm E 96-95, the temperature was 37 °C and humidity 50 %. Gas under pressure 2 MPa and the temperature of 35 °C were used for evaluation of gas permeability according to norm ČSN 64 0115.

3 Results and Discussion

3.1 XRD

XRD spectra were taken only for specimens with nanofillers, pure HIPS and nanofillers; all the spectra are shown in Fig.1. Powders were measured by different measuring technique than composites. Interval of scanning was chosen from 1 to 10 º2Theta, because the most significant peaks around 2 and 5 º2Theta are this area, which identify intercalated/exfoliated structure of nanocomposite.

In the case of Nanofil 5 composites, the second peaks are shifted to lower degrees, which could be due to the partly-exfoliated structure of nanocomposite. On the other hand, Nanofil SE3010 samples have perhaps only intercalated structure.

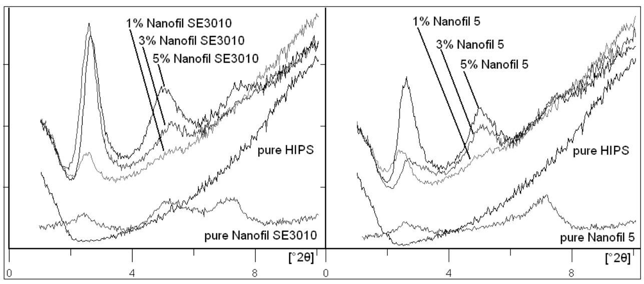

Fig.1 Spectra of nanofilled samples.

3.2 TEM

The transmission electron microscopy observation is presented in Fig.2 A-D. It is possible to see that the dispersion of layered clay fillers Nanofil 5 and Nanofil SE3010 is almost same. Ittercalation was reached in both cases; however, layers are arranged in one direction which means that there is no perfect exfoliation.

In the case of Nanofil 5 (Fig.2D), it can be observed that group of layers are thinner than in case of Nanofil SE3010 (Fig.2B), but both the materials can be consider as nanocomposites.

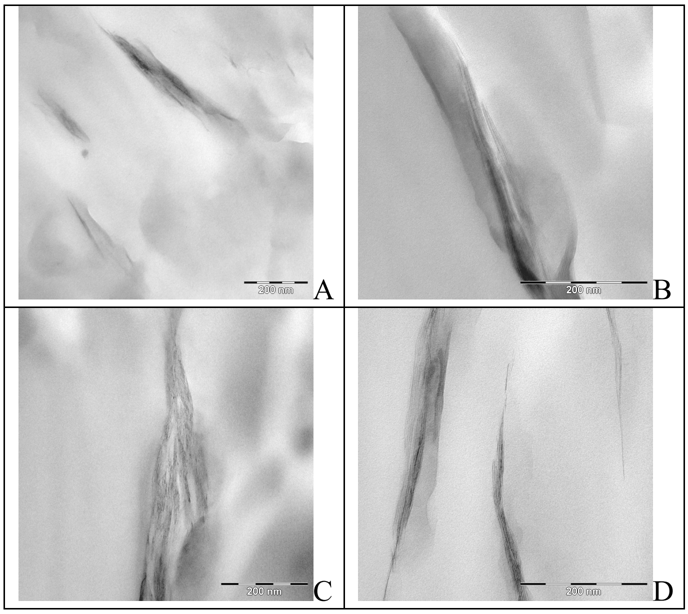

Fig.2 TEM pictures of samples with 3% Nanofil SE3010 (A,B) and Nanofil 5 (C,D).

3.3 Gas permeability

Results from tests of gas permeability were done only for samples 3%-loaded. The zero base line in Fig.3 represents pure HIPS and values are shown in percentage difference of this value.

Samples with Nanofil 5 and Aerosil R812 proved improvement, because their gas permeability for nitrogen and air is about 20 % lower than pure HIPS value. In the case of layered clay nanofiller Nanofil 5, that could be due to the intercalated structure of filler in the polymer matrix, because barrier properties are highly depended on the dispersion of filler. Aerosil R812 has particles of a spherical shape in nanometer dimension, which perhaps protects the gas molecule passing.

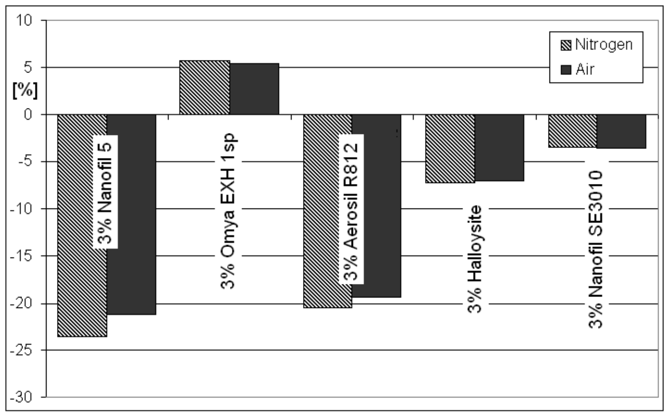

Fig.3 Permeability of samples for nitrogen and air.

3.4 Water vapor permeability

Water vapor permeability test (Fig.4) showed an improvement for almost all filled samples. The values are in a percentage difference of pure HIPS value – the

ISSN: 1792-6211 / ISSN: 1792-6238 ISBN: 978-960-474-248-6

zero base line, like in the case of gas permeability measurements.

There is a relation between loading and consequent permeability for almost any filler. In some cases, certain loading deteriorates barrier property, e.g. 1 % Omya EXH 1sp and 5 % Nanofil SE3010.

The best results are reached by using Aerosil R812 in general and with high loading of Omya EXH 1sp. In contrary, Nanofil 5 samples, which have the best property for gas testing, get only an average improvement for water vapor besides other fillers.

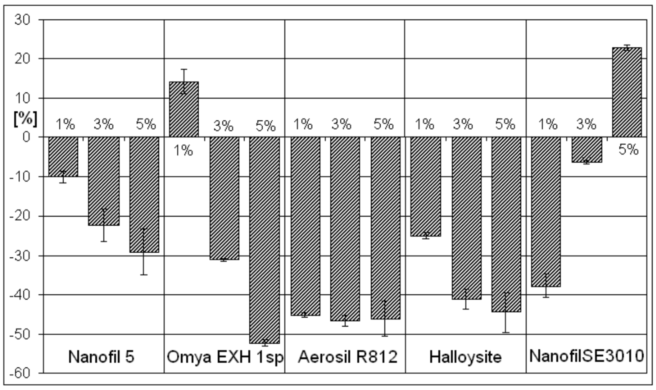

Fig.4 Graf of water vapor permeability.

3.5 Mechanical properties

The obtained results from mechanical properties – resilience and hardness are summarized in Fig.5.

The values of resilience showed significant decrease for all samples. This could be caused by stiffening effect of used fillers. Almost every filler has relation between loading and value of resilience.

The values of hardness have no relation with percentage loading of filler. Majority of samples denotes decrease of values besides pure HIPS.

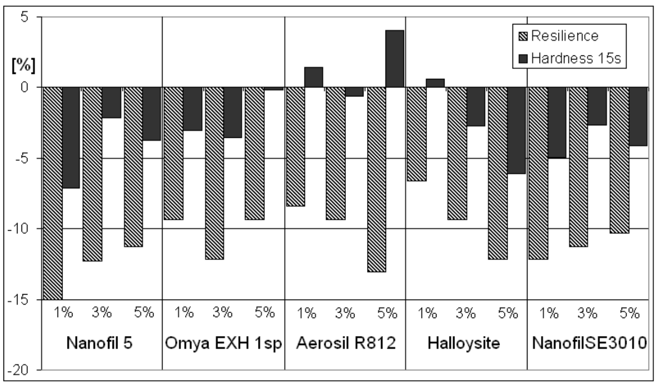

Fig.5 Results of resilience and hardness.

4 Conclusion

Composites with fillers Nanofil 5 and Aerosil R812 approve improvement of barrier properties besides pure HIPS matrix. The gas permeability for nitrogen and air and the water vapor permeability (in the case of Aerosil R812) is about 20 % and 45 % respectively lower than pure HIPS value.

As the XRD spectra show, in the case of clay layered nanofillers Nanofil 5 and Nanofil SE3010 the intercalated structure was perhaps reached.

Although we tested only 3%-loaded samples for gas permeability, other concentration of fillers will be measured in further research.

Acknowledgements

This project was supported by the Academy of Sciences of the Czech Republic (projects KAN 100400701 and AVOZ40500505).

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