Preparation of a new generation porous thermal insulation mass using functional nanomaterials

Dr. J. Ulbikas [a], J. Boženko [a], N. Spirova [a], S. Tučkutė [b]

[a] Industrial applications laboratory of sol-gel technology, CJSC Modern E-Technologies, Taikos str. 7-24, LT-31107, Visaginas, Lithuania, julija@met.lt

[b] Lithuanian Institute of Energy, Breslaujos str. 3 , LT - 44403 Kaunas, Lithuania, simona@hydrogen.lt

ABSTRACT

In this work silica precursor is graft on nanomaterials via a free-radical reaction. The modified nanomaterials have an -OEt functional group which allows us to intercalate the polymer between the layers of expandable graphite and nanoclay. When materials that contain expandable graphite and nanoclay are exposed to a heat source nanomaterials expand and generate a voluminous insulating layer, retardant from the polymer matrix.

The sol-gel technique was applied to modify the nanomaterial and to prepare inorganic and organic hybrid nanocomposites. The morphological properties and elemental composition of the nanocomposites will be examined using XRD (X-Ray diffraction analysis), SEM (scanning electron microscope) and Energy dispersive spectrometry (EDS), respectively.

Keywords: nanomaterials, sol-gel method, elemental composition and morphological properties, scanning electron microscope (SEM)

1 INTRODUCTION

Nanotechnology is presently seen as one of the most promising approaches in the field of materials science towards the development of advanced materials for future engineering applications. Recent and ongoing research on polymer/inorganic nanocomposites has shown dramatic enhancements in thermal, mechanical and chemical properties over the neat polymer without compromising density, toughness, and processibility[1]. This study investigates the effects of different types of nanoparticles on thermal, fire-retardant and mechanical performance of extruded or expanded polystyrene.

Three different types of nanomaterials namely silica nanoparticles (SiO_2 prepared by sol-gel technology), expandable graphite and nanoclay modified with sol-gel technology are considered.

Intumescent flame retardants have been developed rapidly using expandable graphite (EG) and nanoclay (NC)[2-5].

EG is a graphite intercalation compound. The EG can be made through intercalate sulphuric acid into the crystal layer of the graphite. The chemical reaction for the formation of EG is presented as follows[6]:

$$24nC + MH_2SO_4 + ½\ O_2 \longrightarrow C_{24n}(HSO^-_4)\ (m\text{-}1)\ x\ (H_2SO_4) + ½\ H_2O$$

When materials that contain EG are subjected to a heat sourse, EG expand and generate a voluminous insulating layer, retardant flames from the polymer matrix.

The incorporation of a relatively low quantity of (organomodified) nanoclay in the polymer matrix creates a protective layer during combustion. Upon heating, the viscosity of the molten polymer/layered silicate nanocomposites decreases with increasing temperature and facilitates the 45 migration of the clay nanolayers to the surface. Moreover, heat transfer promotes thermal decomposition of the organomodifier and the creation of strongly protonic catalytic sites onto the clay surface, which can catalyze the formation of a stable char residue . Therefore accumulation of the clay on the surface of the material acts as a protective barrier that limits heat transfer into the material, volatilization of combustible degradation products and diffusion of oxygen into the material[7].

And finally, silicon (silica nanoparticles) can be considered to be regarded as an element with enhanced flame retardancy, and has been used in flame retardant system for polymer. Accordingly, as well as improving polymers' thermal and mechanical properties, the silica-based organic-inorganic nanocomposites are expected to exhibit much better flame retardant properties than virginal polymers. The silicon can be easily added into the composites through the sol-gel technique[8].

The sol-gel technique was applied to reactions in the polymer matrix to prepare inorganic and organic hybrid materials. This method has some advantages: it is easy to be controlled by catalyst, it can react at low temperature, the inorganic components will be dispersed uniformly in the polymer matrix [9-11].

The purpose of this study is to examine synergistic effects of expandable graphite and silica on the halogen-free flame retardant properties using sol-gel method. In this work, EG was functionalized using coupling agent

containing silicon to increase the interactive force between organic and inorganic phases. The structure analysis and elemental composition will be characterized by XRD and EDS. The morphological properties of the composites will be examined using SEM.

2 EXPERIMENTAL

2.1. Materials

The polymer used was polystyrene (EPS), which was purchased from Baltic Polystyrene CJSC, Lithuania. Expandable graphite (EG type-250) was supplied by Nordmann, Rassmann GmbH, Germany. Vinyltrietoxysilane (VTES) was purchased from Merck KGaA, Germany. Benzoyl peroxide (BPO) was obtained from Merck KGaA, Germany. Tetrahydrofuran (THF) was supplied by AppliChem, Darmstadt.

2.2. Preparation of EG surface modification

To prepare EG with modified surface, 2 g EG was functionalized with 10 g VTES and 40 ml THF at 61°C by refluxing for 4 h. The free-radical reaction was initiated by BPO. EG-VTES was washed using THF 4 times and then dried overnight at room temperature.

2.3. Preparation of EPS/EG-VTES composites

The polystyrene (EPS) was melted under the pressure at 115-125° C temperature. In melted mass of polystyrene were added 10, 15 wt % EG-VTES, 2 wt % Nanoclay and 2 wt % Silica nanoparticles. The resulting product was granulated and cooled at room temperature.

2.4. Reaction schemes

The composite materials were prepared as described in Figure 1-2 [12].

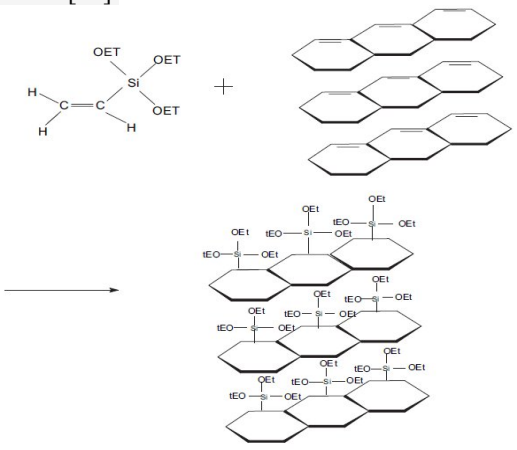

Figure 1. Modification of nanomaterials by sol-gel technology

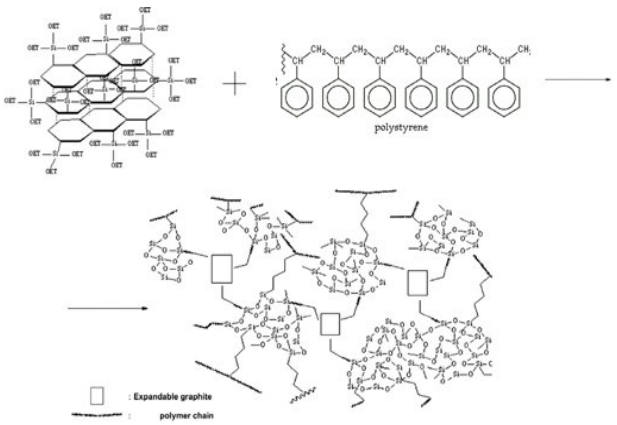

Figure 2. Reaction process of polystyrene and modified nanomaterials through extrusion process

2.5. X-Ray difraction analysis (XRD)

X-ray diffraction (XRD, D8 Discover (Bruker AXS GmbH) standard Bragg–Brentano focusing geometry with an error of 0.0001°) in a 20–70° range using the Cu Kα1 (λ=0.1540562 nm) radiation.

2.6. Morphological properties

The morphology of the fractured surface of the composite was examined using a scanning electron microscope (SEM) (JEOL JSM-5600).

2.7. Energy dispersive spectrometry (EDS)

The energy dispersive spectrometry (EDS, Bruker AXS Microanalysis GmbH) analysis was used to determine the elemental composition of formed composites.

3 RESULTS AND DISCUSSION

3.1. Elemental composition analysis

The elemental composition analysis was characterized by Energy dispersive spectrometry (EDS). Fig. 3(a) displays spectrum of EG before modification with sol-gel technology. The EDS spectrum shows a structured pure graphite – elemental C (carbon).

Fig. 3(b) shows EG with modified surface. On the spectrum we see – elemental C (carbon), O (oxygen) and S (sulfur). We notice that free-radical reaction has occurred successfully and the EG surface was modified.

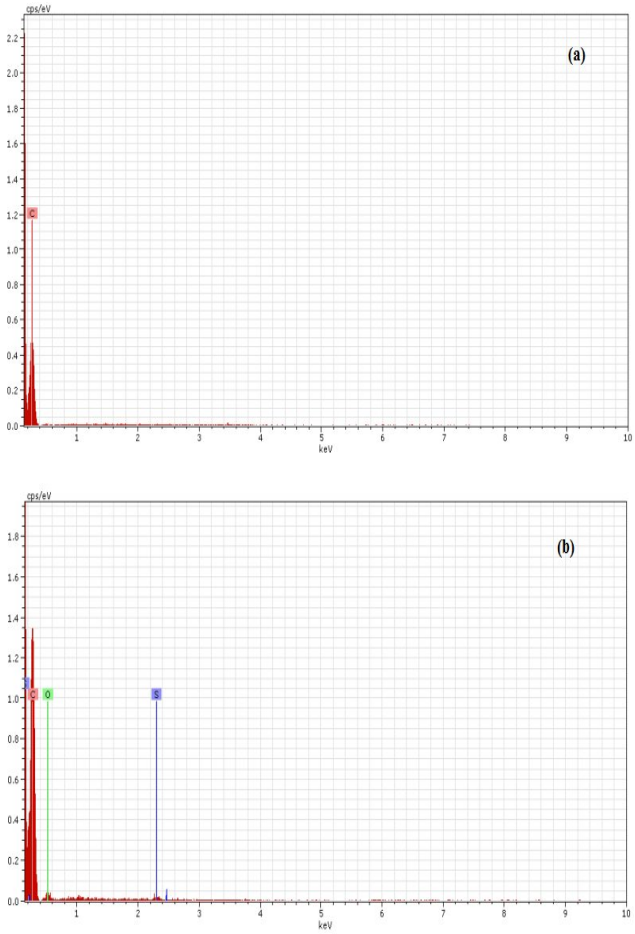

Figure 3. EDS spectrum of the (a) pure EG type-250 and (b) modified EG type-250

The elemental composition analysis measurements are summarized in Table 1 and 2.

Table 1. Elemental microanalysis of pure EG type-250

Element	series	[wt.%]	[norm. wt.%]	[norm. at. %]
Carbon	K-series	99,999	100	100
	Sum:	99,999	100	100

Table 2. Elemental microanalysis of modified EG type-250

Element	series	[wt.%]	[norm. wt.%]	[norm. at.%]
Carbon	K-series	91,62923	91,63106	94,28099
Oxygen	K-series	6,442879	6,443008	4,976747
Sulfur	K-series	1,925889	1,925927	0,742259
	Sum:	99,998	100	100

3.2. Morphological properties

Fig. 4 displays SEM microphotographs of EG type-250 before surface modification with sol-gel technology. The expandable graphite has a layered structure and agglomerate to form a sheets. The carbon flakes are so compactly folded that the polymer can't enters the slots of the graphite sheets.

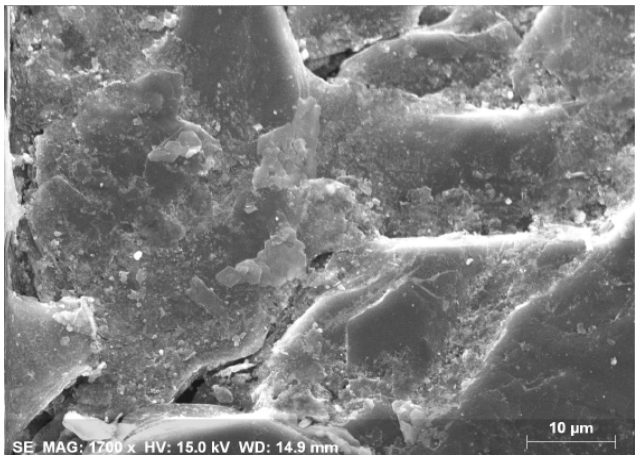

Figure 4. The SEM microphotographs of EG type-250 before surface modification

Fig. 5 displays the expandable graphite type-250 after surface modification with sol-gel technology. As we can see, the graphite surface has changed. The surface becomes more layered compared with unmodified EG. This allows us to assume that the inorganic components will be dispersed uniformly in the polymer matrix.

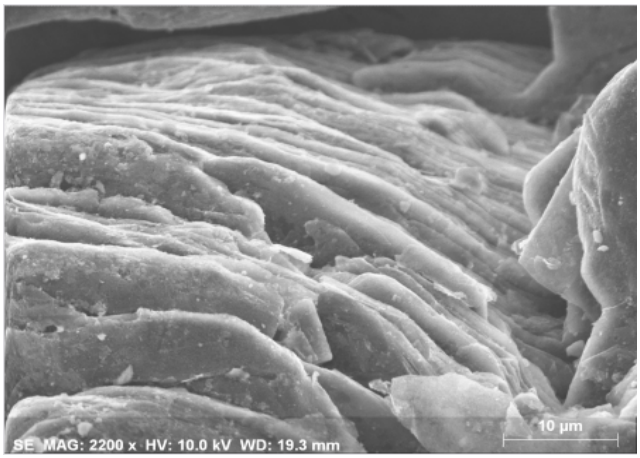

Figure 5. The SEM microphotographs of EG type-250 after surface modification

Fig. 6 displays the overview of EPS/EG/NC nanocomposite after burning. The SEM microphotographs demonstrate that expandable graphite layer works as an insulating layer to reduce the heat transfer because of the

large volume expansion. It fully allows to protect the surface of the polymer from the flame. EG expansion is caused by redox process between H_2SO_4 and the graphite that originates the blowing gases [13].

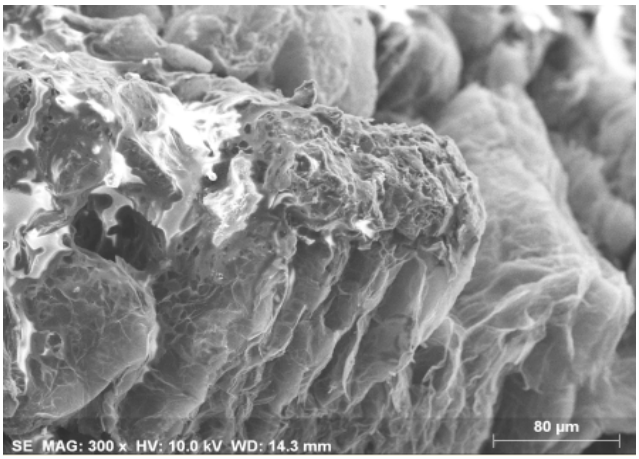

Figure 6. The SEM microphotographs of the nanocomposite after burning: EPS/EG/NC

3.3. X-ray diffraction analysis

Diffraction analysis was performed on the surface of the nanocomposite EPS/EG/NC after burning. The spectrum shows that the nanocomposite surface is completely covered with layers of graphite (carbon). The graphite layers formation on the surface of the polymer nanocomposite, protect the polymer from degradation, prevent the release of toxic gases into the atmosphere thereby blocking the spread of fire.

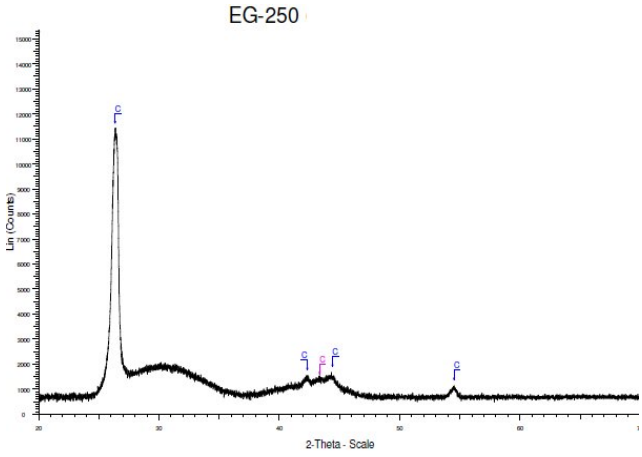

Figure 7. XRD diffraction spectrum of the nanocomposite after burning: EPS/EG/NC

4 CONCLUSIONS

The sol-gel technology has been applied to modify the nanomaterials such as expandable graphite type-250 and nanoclay. The EG and NC were functionalized by vinyltrietoxysilane via free-radical reaction. The structure and morphology of the obtained products was examined by SEM and EDS analysis. After modification surface of expandable graphite becomes more layered, it allows us to assume that the inorganic components will be dispersed uniformly in the polymer matrix. After burning nanocomposite was seen that expandable graphite layer works as an insulating layer to reduce the heat transfer because of the large volume expansion. It protect the polymer from degradation, prevent the release of toxic gases into the atmosphere thereby blocking the spread of fire.

REFERENCES

[1] Materials Science and Engineering: Enhancement in thermal and mechanical properties of polyurethane foam infused with nanoparticles. M.C. Saha, Md.E. Kabir, S. Jeelani. 28 June 2007

[2] Modesti M, Lorenzetti A, Simioni F, Camino G. Expandable graphite as an intumescent flame retardant in polyisocyanurate polyurethane foams. Polym Degrad Stab 2002;77:195–202.

[3] Duquesne S, Le Bras M, Bourbigot S, Delobel R, Camino G, Eling B, et al. Thermal degradation of polyurethane and polyurethane/expandable graphite coatings. Polym Degrad Stab 2001;74:493–9.

[4] Xie RC, Qu BJ. Expandable graphite systems for halogen-free flame retarding of polyolefins. I. Flammability characterization and synergistic effect. J Appl Polym Sci 2001;80:1181–9.

[5] Bian XC, Tang JH, Li ZM, Lu ZY, Lu A. Dependence of flame-retardant properties on density of expandable graphite filled rigid polyurethane foam. J Appl Polym Sci 2007;104:3347–55.

[6] Zabel H, Solin SA. Graphite intercalation compounds I – structure and dynamics. Berlin: Springer-Verlag Press; 1990.Weil ED, Levchik SV Flame retardants in commercial use or development for polyolefins. Fire Sci 2008;26:5–43.

[7] Use of RAFT technique as an efficient method to synthesise well-defined polymer-clay nanocomposites with improved properties. Dissertation 2008, Austin Samakande.

[8] Li G, Liang G, He T, Yang Q, Song X. Effects of EG and $MoSiO_2$ on thermal degradation of intumescent coating. Polym Degrad Stab 2007;92:569–79.

[9] Yang F, Ou Y, Yu Z. Polyamide 6/silica nanocomposites prepared by in situ polymerization. J Appl Polym Sci 1998;69:355–61.

[10] Song X, Wang X,Wang H, Zhong W, Du Q. PMMA–silica hybrid thin films with enhanced thermal properties prepared via a non-hydrolytic sol–gel process. Mater Chem Phys 2008;109:143–7.

[11] Hsiue GH, Liu YL, Liao HH. Flame-retardant epoxy resins: an approach from organic–inorganic hybrids nanocomposites. J Polym Sci A Chem 2001;39: 986–96.

[12]Polymer degradation and stability. Synthesis,characterization,flame retardance and thermal properties of halogen-free expandable graphite/PMMA composites prepared from sol-gel method. 2008

[13] Camino G, Duquesne S, Delobel R, Eling B, Lindsay C, Roels T. In: Nelson GL, Wilkie CA, editors. Fires and polymers: materials and solutions for hazard prevention. Washington, DC: ACS Publishers; 2001. p. 90–109 (symposium series no. 797).