

Shape and Size of Filler vs. Mechanical Properties and Flammability of Polystyrene Nanocomposites

Dagmar Merinska, Zuzana Dujkova, Hana Kubisova, Petr Svoboda, Miroslav Slouf
Tomas Bata University in Zlin, Nám. TGM 275, Zlín
Institute of macromolecular chemistry in Prague, Heyrovského nám. 2, Praha 6
Czech Republic
merinska@ft.utb.cz

Abstract: - Presented work deals with the evaluation of the connection between the shape of (nano)filler and the polystyrene (nano)composites. Fillers and nanofillers with various type of particles (spherical, tubes, layered...) were chosen for the preparation of PS composites and nanocomposites. All samples were prepared by the compounding i.e. by the mixing in the melt of PS. Morphology and the level of distribution was evaluated by XRD and TEM. Next flammability and mechanical properties were observed. The best result was achieved with the layered mineral nanofiller Cloisite Na+.

Key-Words: polystyrene, composite, nanocomposite, flammability, fire retardation

1 Introduction

Clay/polymer nanocomposites including polystyrene (PS) ones have been studied extensively during the last two decades, because they are supposed to obtain improved properties in the comparison with the neat polymer matrix [1-6]. Polystyrene is a commonly used polymer with various applications, e.g. insulation, packaging, in household and in automotive industry. This is the reason why polystyrene composites and later nanocomposites were studied because of the possibility of PS properties improvement [7-11].

The main problem of polystyrene is high flammability with generation of large amounts of carbon black and low thermal stability [12-16].

Nowadays the solution of this problem of high PS flammability is performed by the use of several types of additives, mainly having the chemical effect. Unfortunately, many of them are toxic and step by step they became banned from using as flame retardants. This is a reason why there is an on-going effort to find the new substances capable to substitute the toxic ones [9-10, 17]. The different way how to lower PS flammability does not have to be a chemical one, but a physical one – introducing these types of additive which will create some physical barrier between oxygen and polymer matrix. In case of nanocomposites based on polymer matrix and layered clays there is a theory about the possibility of lowering the flammability which is caused by the layered shape of clay mineral filler, especially montmorillonite (MMT). It is believed that exfoliated MMT particles homogenously dispersed in the polymer matrix are able to create a solid inflammable layer on the surface that protects polymer matrix from further burning [18-19]. There are other clay minerals, such as

magadiite or fluorohectorite that have a similar affect on the flammability [20-21].

Exciting area of research is search for possible synergic effect of common types of flame retardants with clay nanofillers [22].

Flammability measurement generally can be carried out by several different methods, for example by the evaluation of limiting oxygen index, TGA analysis, increased oxygen index etc. [14, 19, 23]. The most frequent method is a cone calorimetry [9, 17-18].

This work is focused on the evaluation of the influence of size and shape of filler (nanofiller) on the flammability and mechanical properties. Various types of fillers were tested.

2 Experimental

2.1 Materials

Commercial polystyrene KRASTEN® 174 from SYNTHOS Kralupy a.s., Czech Republic was used as a polymer matrix. Unmodified clay CloisiteNa+ (Southern Clay Chemistry, US), and organically modified clays Nanofil 9 and Nanofil 5 (Südchemie, Germany) were used as layered nanofillers. Modified silica Aerosil R 812 (Degussa) and micromilled calcite OMYA EXH 1sp (Calplex) were used as fillers with spherical shape. And organosilicate nanotubes Halloysite NT (Sigma-Aldrich) were used as nanofiller with the particles in the shape of long thin tubes.

2.2 Preparation of composites and specimens

Composites were prepared by mixing and compounding in a laboratory twin-screw extruder Berstordff ZE25 with six heating zones and the L/D ratio being 38. Temperature was 170 °C and the speed of the screws was 100 rpm. All components for every sample were premixed in the laboratory mixer KLAD for 15 min. All mixtures were extruded two times.

In order to prepare specimens for the mechanical properties evaluation the pellets were molded according to ISO 294-1 at the equipment BATTENFELD 500 CD+, melt temperature 220 °C, form temperature 45 °C. Flammability measurement was performed on the same type of specimens as the ones for mechanical properties. The dimensions were 127 x 13 x 3,2 mm.

The XRD measurement was performed on the specimens prepared by pressing in a hot press at for 3 min at 210 °C followed by cutting of a circle shape. The thickness was 1 mm.

2.3 Instrumentation

The level of exfoliation in the prepared samples after compounding process was measured by XRD patterns. Compounded samples were analyzed by XRD powder diffractometer (INEL) equipped with the curved position sensitive detector CPS 120 (120° 2 θ), reflection mode with a germanium monochromator (Cu α 1 radiation). Samples were placed into holder and exposed for 2000s.

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

The flammability measurement was carried out according to STD N 60695-11-10.

Mechanical properties were measured according to ISO 527-2/1A/X on the Zwick 145665. All presented data are the arithmetic average taken from 10 measurements.

The impact strength measurement was done according to ISO 179-2/1eU on the machine Zwick-Roell with 5 J hammer. Again, all presented data are the arithmetic average taken from 10 measurements.

3 Problem Solution

3.1 XRD

The XRD analysis was used for the evaluation of the level of MMT exfoliation in the PS matrix in case of clay nanofillers Cloisite and Nanofil. The results are

summarized in the Fig. 1. From the XRD patterns it is clear that the highest level of exfoliation was achieved in case of Cloisite Na⁺, where the peak belonging to the MMT almost disappeared. Patterns of Nanofils show that the significant portion of MMT particles did not exfoliate. These results are reflected in the following properties.

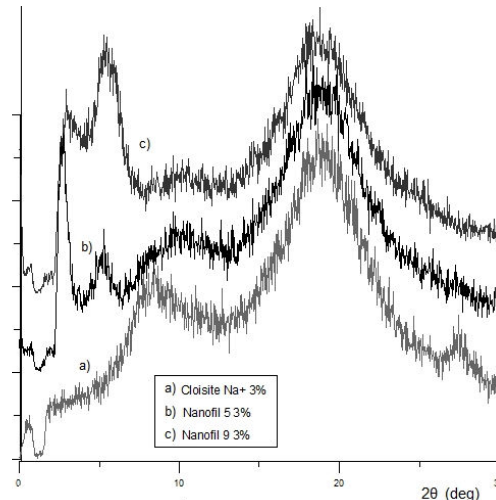
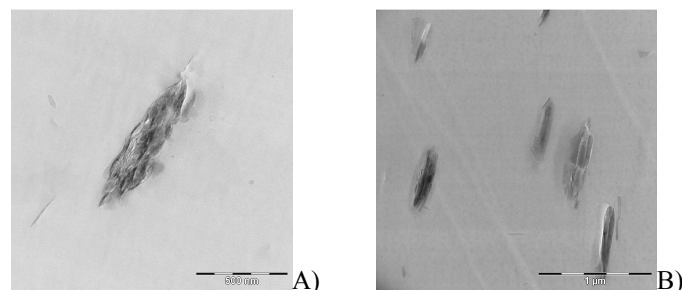


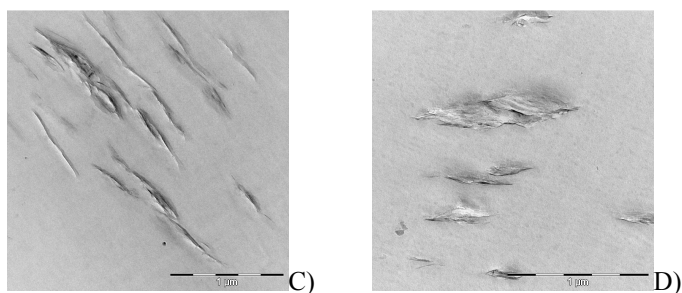
Fig. 1. XRD patterns of Cloisite and Nanofil/PS nanocomposite (layered type of nanofiller).

3.2 TEM

TEM observation is presented by Fig. 2 A-D. It is possible to see that in case of layered fillers for Nanofil 5 (Fig. 2 C) there was achieved the best dispersion in the PS matrix. The worse was found for unmodified Cloisite Na⁺ (Fig. 2A). In comparison of Nanofil 5 and Nanofil 9 (Fig. 2 D) samples, picture of Nanofil 5 shows better intercalation than the picture of Nanofil 9. However, layers are arranged in one direction what means that there is no perfect exfoliation.

Fig 2 B represents the picture of the sample of Halloysite tubes. It is possible to say that there the filler particles are not regularly dispersed.





the neat PS matrix (Krasten 174). The reason of this form of expression is the differences in obtaining the data of compared materials. These values were not constant every day but they varied, probably because of the environmental conditions (atmospheric press, humidity etc.)

Table 1.

Fig 2. TEM pictures: A) Cloisite Na+, B) Halloysite NT, C) Nanofil 5, D) Nanofil 9

3.3 Flammability

Results of the flammability observations are summarized in the Table 1 (visual description) and Fig. 3. Values in

The results indicate that the burning speed is higher in comparison with the pure PS matrix. From this point of view there is no relation with the shape or size of filler. The only interesting result was the difference in the values for differently modified MMT. Only the nanofiller Nanofil 5 brought significant reduction in the melt dripping (see Table 1). Other fillers did not cause this dripping prevention. It will be a topic of the following study whether this effect was caused by higher MMT interlayer of Nanofil 5 or if the most important factor is the level of exfoliation in MMT particles.

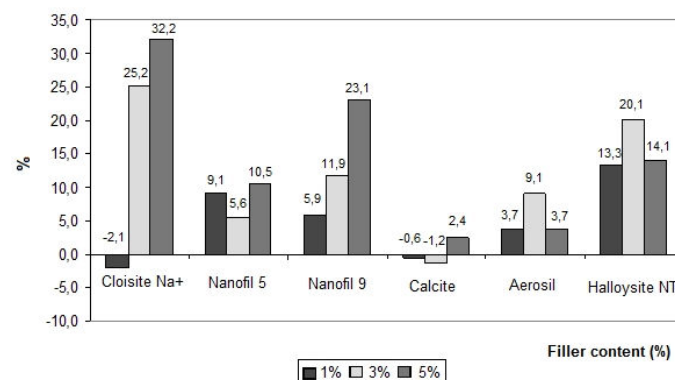


Fig. 3. Flammability – the relative speed of the burning

Filler/loading	1 %	3 %	5%
Cloisite Na+	The same behaviour as a nonfilled PS - at the burning it drips off. No significant carbonized residue is present after the body burns.		
Nanofil 5	Dripping off of the melt is slower. Partly creation of carbonized residue.	The melt does not drip off. The carbonized residue is created.	The melt does not drip off. Carbonized skeleton rests on the raster after PS burns.
Nanofil 9	The same behaviour as a nonfilled PS - at the burning it drips off. No significant carbonized residue is present after the body burns.		
Micr. Ca₂CO₃	The same behaviour as a nonfilled PS - at the burning it drips off. No significant carbonized residue is present after the body burns.		
Silika (Aerosil)	The same behaviour as a nonfilled PS - at the burning it drips off. No significant carbonized residue is present after the body burns.	Dripping off of the melt is slower. Partly creation of carbonized residue - not so significant as in case of Nanofil 5.	Significantly slower dripping off of the melt. The carbonized residue is created – not so significant as in case of Nanofil 5.
Halloysite nanotubes	The same behaviour as a nonfilled PS - at the burning it drips off. No significant carbonized residue is present after the body burns.		

the graph mean an increase or decrease in the burning speed of the specimens according to the filler type. The values are expressed as a change (in %) with respect to

3.4 Mechanical properties

In the evaluation of mechanical properties and their dependency on the size and shape of filler, the tensile strength, modulus and impact strength were measured.

The results are summarized in Figs. 4-6. The values of modulus measurement (Fig. 4) show that the modulus is the highest in case of layered nanofillers, lower for spherical ones and the lowest for nanotubes. Generally, the values increase with increasing filler content. At this point it is possible to say that there is a connection between the modulus and the shape of filler because the same shape exhibits similar behaviour and values.

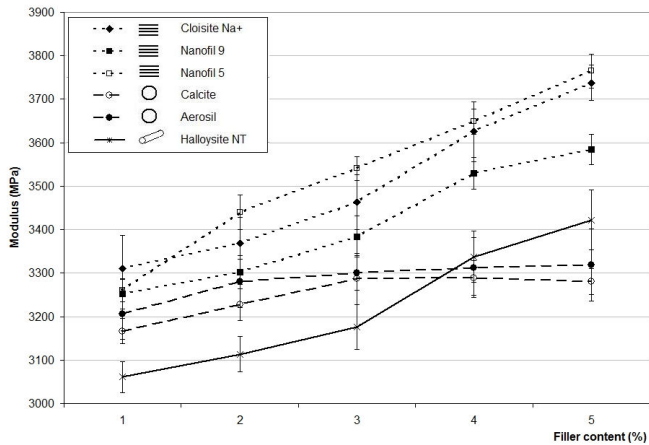


Fig. 4. Mechanical properties – modulus

The evaluation of tensile strength brought a little bit different data. Firstly, the values decrease with increasing filler content. This fact could be expected by worse exfoliation at the higher loading caused by the tendency of filler particles to agglomerate. The highest tensile strength was found for Cloisite Na⁺ which showed the best exfoliation (see XRD). In fact only composites containing this filler showed increase in tensile strength with increasing filler content (in the range 1-2 wt%).

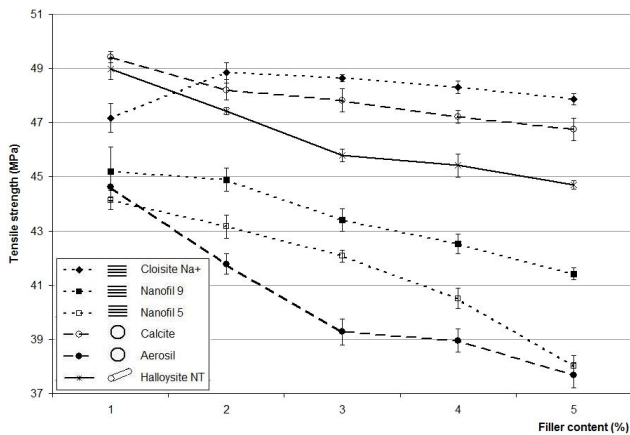


Fig. 5. Mechanical properties – tensile strength

The similar result to the tensile strength measurement was obtained in case of the evaluation of the impact strength. Again the best results were found for the sample PS/Cloisite Na⁺. In contrast to the previously discussed property in this graph all curves have the decreasing tendency with the increasing filler content. All other fillers exhibited significantly lower values of impact strength. This again can be explained by the lower level of exfoliation.

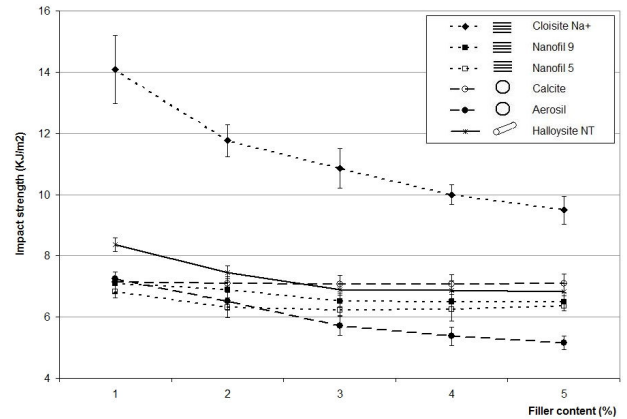


Fig. 6. Mechanical properties – impact strength

4 Conclusion

Samples of polystyrene composites containing fillers with various size and shapes of the particles were prepared. The concentration of fillers was from 1 to 5 wt. %. The influence of the size, shape and concentration on flammability, barrier and mechanical properties was studied.

TEM observation confirmed intercalation and partial exfoliation of layered nanofillers.

Flammability study did not show any connection between the size and shape of the filler particles and the flammability. None of the investigated fillers decreased the flammability significantly. The only interesting result was found for Nanofil 5 when the melt dripping was reduced.

Mechanical properties exhibited the connection of shape and size vs. properties only for the evaluation of modulus where the highest data were found for the layered fillers. Also the values of tensile strength and impact strength are the highest for the layered type of filler, however, spherical particles and particles with other shape exhibited lower mechanical properties.

To sum up, the most significant effect on of filler on measured properties was found for the layered type of nanofiller Cloisite Na⁺.

ACKNOWLEDGEMENTS

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

References:

1. K.Chen, M.A. Susner, S. Vyazovkin, Effect of the brush structure on the degradation mechanism of polystyrene-clay nanocomposites, *Macromolecular Rapid Communications*, 26, 9, 2005, pp. 690-695
2. K.Chen, S. Vyazovkin, Mechanistic differences in degradation of polystyrene and polystyrene-clay nanocomposite: Thermal and thermo-oxidative degradation, *Macromolecular Chemistry and Physics*, 207, 6, 2006, pp. 587-595
3. W.H.Awad, High-throughput method for the synthesis of high performance polystyrene nanocomposites, *Polymer-Plastics Technology and Engineering*, 45, 10, 2006, pp. 1117-1122
4. A.B.Morgan, J.W.Gilman, Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: A comparative study, *J. Appl. Polym.Sci.*, 87, 8, 2003, pp. 1329-1338
5. J.M. Yeh, C.P. Chin, Structure and properties of poly(o-methoxyaniline)-clay nanocomposite materials, *J. Appl. Pol. Sci.*, 88, 4, 2003pp. 1072-1080
6. S.J.Ahmadi, Y.D. Huang, W. Li, Synthetic routes, properties and future applications of polymer-layered silicate nanocomposites, *J. Mat. Sci.*, 39, 6, 2004, pp. 1919-1925
7. S.Su, D.D. Jiang, C. A. Wilkie, Novel polymerically-modified clays permit the preparation of intercalated and exfoliated nanocomposites of styrene and its copolymers by melt blending, *Pol. Degr. Stab.*, 83, 2, 2004, pp. 333-346
8. K.Chen, C.A. Wilkie, S. Vyazovkin, Nanoconfinement revealed in degradation and relaxation studies of two structurally different polystyrene-clay systems, *J.Phys. Chem.*, 111, 2007, pp. 12685-12692
9. G. Chigwada, D.Y. Wang, C.A. Wilkie, *Pol. Degr. Stab.*, 91, 4, 848-855, (2006).
10. G. Chigwada, D.Y. Wang, D.D. Jiang, C.A. Wilkie, Styrenic nanocomposites prepared using a novel biphenyl-containing modified clay, *Pol. Degr. Stab.*, 91, 4, 2006, 755-762
11. S.Nazarenko, P. Meneghetti, P. Julmon, Gas barrier of polystyrene montmorillonite clay nanocomposites: Effect of mineral layer aggregation, *J. Pol. Sci., Part B: Pol. Phys.*, 45, 2007, pp. 1733-1753
12. A.B. Morgan, J.W.Gilman, R.H.Harris, Flammability of polystyrene-clay nanocomposites, *Abstracts of papers of ACS*, 220, 64-PMSE Part 2, 2000, pp. U338-U338
13. A.B. Morgan, Flame retarded polymer layered silicate nanocomposites: a review of commercial and open literature systems, *Pol. Adv. Techn.*, 17, 4, 2006, pp. 206-217
14. S.Bourbigot, S. Duquesne, C. Jama, Polymer nanocomposites: How to reach low flammability? *Macromol. Symp.*, 233, 2006, pp. 180-190
15. F.M. Uhl, C.a. Wilkie, Polystyrene/graphite nanocomposites: effect on thermal stability, *Pol. Degr. Stab.*, 76, 1, 2002, 111-122
16. M.H. Kim, C.I. Park, W.M. Choi, Synthesis and material properties of syndiotactic polystyrene/organophilic clay nanocomposites, *J. Appl. Pol. Sci.*, 92, 4, 2004, pp. 2144-2150
17. A.B.Morgan, L.L. Chu, J.D. Harris, A flammability performance comparison between synthetic and natural clays in polystyrene nanocomposites, *Fire and Materials*, 29, 4, 2005, 213-229
18. A.B. Morgan, R.H. Harris, T. Kashiwagi, Flammability of polystyrene layered silicate (clay) nanocomposites: Carbonaceous char formation, *Fire and Materials*, 26, 6, 2002, 247-253
19. J.W. Gilman, R.H. Harris, J.R. Shields, A study of the flammability reduction mechanism of polystyrene-layered silicate nanocomposite: layered silicate reinforced carbonaceous char, *Polym. Adv. Techn.*, 17, 4, 2006, pp. 263-271
20. D.Y. Wang, D.D. Jiang, J. Pabst, Polystyrene magadiite nanocomposites, *Pol. Eng. Sci.*, 44, 6, 2004, 1122-1131
21. J.W. Gilman, C.L. Jackson, A.B. Morgan, Flammability properties of polymer - Layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites, *Chem. Mater.*, 12, 7, 2000, pp. 1866-1873
22. G. Chigwada, C.A. Wilkie, Synergy between conventional phosphorus fire retardants and organically-modified clays can lead to fire retardancy of styrenics, *Pol. Degr. Stab.*, 81, 3, 2003, pp.551-557
23. F. Yang, R. Yngard, g.L. Neldon, Flammability of polymer-clay and polymer-silica nanocomposites, *J. Fire Sci*, 23, 3, 2005, pp. 209-226