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Nanoparticles of γ-Al_2O_3 as perspective fillers of thermoplastic polymers improving their barrier properties[**)]

Summary — The preliminary results of preparation of γ-Al_2O_3 nanoparticles occurring in special lamellar form were presented. The filler form should advantageously influence the barrier properties of the thermoplastic polymers, filled with such nanofillers.

Key words: alumina, nanoparticles, morphology, fillers of polymers, barrier properties.

NANOCZĄSTKI γ-Al_2O_3 JAKO PERSPEKTYWICZNE NAPEŁNIACZE POLIMERÓW TERMOPLASTYCZNYCH POLEPSZAJĄCYCH ICH WŁAŚCIWOŚCI BARIEROWE

Streszczenie — Przedstawiono wstępne wyniki dotyczące otrzymywania nanocząstek γ-Al_2O_3 występujących w specyficznej postaci płytkowej (rys. 2 i 3), która powinna korzystnie wpływać na właściwości barierowe polimerów termoplastycznych napełnianych takimi nanocząstkami (rys. 1).

Słowa kluczowe: tlenek glinu, nanocząstki, morfologia, napełniacze polimerów, właściwości barierowe.

The very large commercial importance of polymers has been driving an intense investigation in polymers combined with particles, fibers etc. [1—3]. For instance, enhanced mechanical properties [4, 5], barrier properties [6], ionic conductivity [7], thermal stability and fire retardancy [8—10] of so received materials relative to the virgin polymer have been observed.

The interest of the scientific community in nanocomposites in particular is due to their remarkable properties in comparison to conventional composites. More specifically, barrier enhancement is gaining more and more scientific interest. The barrier function can be incorporated into a polymer matrix in two different ways — either by fixing a layer of barrier material to the polymer or by mixing the barrier material into the polymer. The mixing of a high-barrier material into the matrix of a polymer leads to an increase in effective path length for the diffusing compound and thereby to an improvement in barrier performance [11]. The high-barrier material can be a polymer or an inorganic filler.

The present paper starts with an outline of strategies to improve barrier technologies. Subsequently, we suggest a promising development in this field: a new method to synthesize inorganic fillers (γ-Al_2O_3) with a specific platelet morphology.

BARRIER TECHNOLOGIES

Over the past few years, there has been a rapid development in the area of new barrier technologies. The innovations go along five major lines: (a) thin, transparent vacuum-deposited coatings (SiO_x or hydrocarbon films on different substrates) [12]; (b) new barrier polymers (thermoplastic epoxy resins) [13]; (c) blends of expensive barrier polymers and inexpensive standard polymers [14]; (d) organic barrier coatings and adhesives (hyperbranched coatings) [15]; and (e) nanocomposite materials (dispersion of the filler in the molten material) [16]. In the field of barrier technology, the term "nanocomposites" refers to polymers filled with small inorganic particles with high aspect ratio. Concerning the barrier enhancement technologies, an improvement can be obtained by increasing the tortuosity of the diffusion path, and the result is strongly dependent on the morphology of the fillers, as shown in Fig. 1. Platelet particles (B) — the most common are clay minerals — enhance the barrier properties of a polymer according to a tortuous path model, developed by Neilson [17], in which the platelets obstruct the passage of gases and other permeants through the polymer matrix.

OWN RESULTS

In the past decade, one of the most intensively studied composite systems was that based on organic poly-

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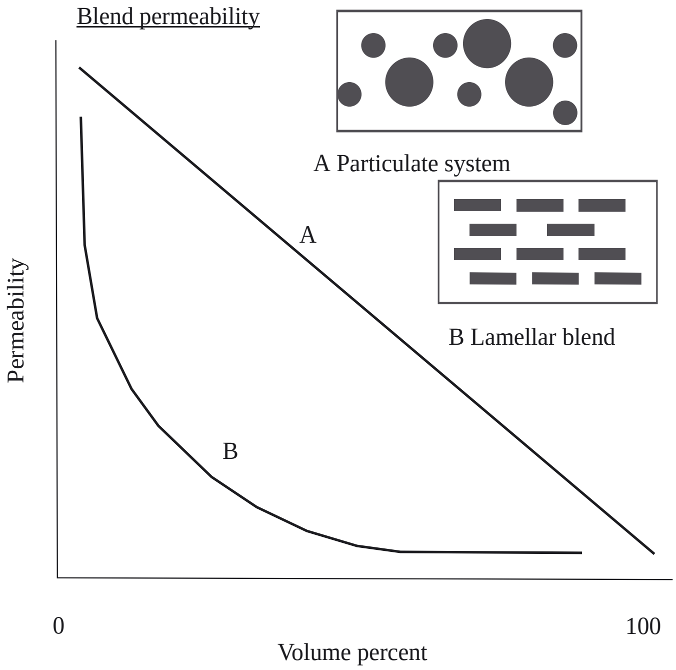

Fig. 1. Schematic illustration of the permeability as a function of the morphology of the fillers

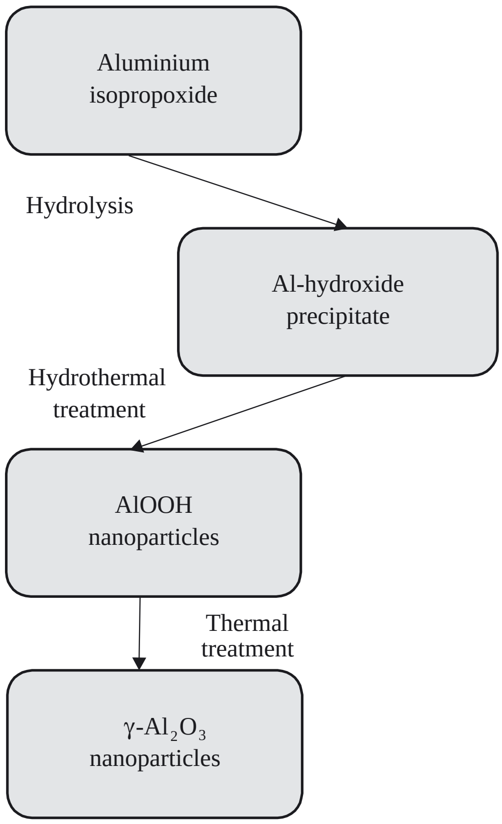

Fig. 2. Schematic overview of the γ-Al_2O_3 nanoparticles synthesis procedure

mers and inorganic clay minerals consisting of silicate layers. The principle used in clay/polymer nanocomposites is to separate not only the clay aggregates but also the individual silicate layers. Hence, we have successfully applied a new method to synthesize inorganic nanofillers, more specifically γ-Al_2O_3, with a platelet morphology similar to clay minerals and, moreover, low aglomeration degree. Nanoparticles of γ-Al_2O_3 were synthesized using the procedure schematically presented in Fig. 2 and comprised morphologies in which the fundamental unit is 30 nm to 100 nm as shown in Fig. 3.

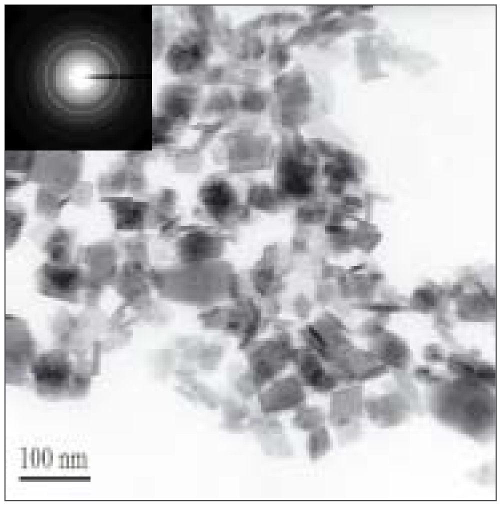

Fig. 3. TEM micrographs of γ-Al_2O_3 powder. Inset: electron diffraction pattern of gamma-alumina (investigation with a Philips CM12 transmission electron microscopy TEM using an accelerating voltage of 120 kV)

Preliminary studies on γ-Al_2O_3 nanoparticles present in a thermoplastic matrix showed that agglomerates were formed and that barrier enhancement was not yet satisfactory, due to the lack of interfacial affinity between the gamma-alumina nanoparticles and the polymer matrix. For this reason, the following key issues need to be further investigated in order to improve the nanoparticle dispersion: the process of γ-Al_2O_3 incorporation into the polymer matrix, the nanoparticle surface treatment and the optional use of dispersing aids.

CONCLUSION

In summary, one of the big new areas of development is in combining new nanomaterials with thermoplastics in order to improve barrier properties. A new and entirely aqueous method has been successfully developed for the synthesis of gamma-alumina nanoparticles with a regular platelet shape. The introduction of these metal oxide nanoparticles as possible barrier material is a promising topic, but still a lot of research is needed to develop nanocomposite systems with optimal performance. Further research on these approaches is expected to lead to better materials.

REFERENCES

1. Dvir H., Gottlieb M., Daren S.: *Composites Sci. Technol.* 2003, **63**, 1865.

2. Weidenfeller B., Höfer M., Schilling F. R.: *Composites Part A* 2004, **35**, 423.
3. Demjén Z., Pukanszky B., Nagy J.: *Composites Part A* 1998, **29A**, 323.
4. Da Silva A. L. N., Rocha M. C. G., *et al*.: *Polym. Test.* 2002, **21**, 57.
5. Pawlak A., Morawiec J., Piotrowska E., Galeski A.: *Polimery* 2004, **49**, 240.
6. Jang J., Lee O. K.: *Polymer* 2004, **45**, 1599.
7. Singh T. K., Bhat S.: *J. Power Sources* 2004, **129**, 280.
8. Filho F., Melo T., Rabello M., *et al*.: *Polym. Degrad. Stabil*. 2005, **89**, 383
9. Kędzierski M., Penczek P.: *Polimery* 2004, **49**, 801.
10. Nour M. A., Hassanien M. M.: *Polimery* 2005, **50**, 371.
11. Lange J., Wyser Y.: *Pack. Technol. Sci.* 2003, **16**, 149.
12. Erlat A. G., Spontak R. J., *et al*.: *J. Phys. Chem*. 1999, **103**, 6047.
13. Brennan D. J., Silvis H., *et al*.: *Macromolecules* 1995, **28**, 6694.
14. Faisant J., Ait-Kadi A., *et al*.: *Polymer* 1998, **39**, 533.
15. Lange J., Stenroos E., *et al*.: *Polymer* 2001, **42**, 7411.
16. Gusev A., Lusti H.: *Adv. Mater.* 2001, **21**, 13.
17. Neilson L. E.: *J. Macromol Sci.* 1967, **A1**, 929.