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Structure and properties of polyurethane nanocomposites modified by dibutyl phosphate boehmite

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The paper reports on the application of the quantitative analysis of images to describe morphological properties of nanocomposites composed of polymers and organically modified boehmite. Images of boehmite, as well as the fracture and cut surfaces of composites, were obtained using high resolution electron microscopy technique and atomic force microscopy. Quantitative analysis of the images of fracture structure obtained by the SEM technique allowed one to explain the mechanism of changes of the mechanical properties of polyurethane nanocomposites. Parameters of stereological analysis were used to evaluate the diameter of the agglomerates of nanofillers and the analysis of relationships between the nanocomposite structure and properties.

Key words: *image analysis; nanocomposite; boehmite; polyurethane; dibutyl phosphate; thermal analysis*

1. Introduction

Polymer composites are manufactured for many applications such as automobiles, aerospace functions, etc. One of the dimensions of the fillers of new materials is of the order of a nanometres. The combination of mechanical, thermal and electrical properties of a material and low concentration of the filler necessary to produce changes in the polymer matrix, has generated much interest in the field of nanocomposites. The nanocomposites can be fabricated and processed in ways similar to those employed for conventional polymer composites. The transition from microparticles to nanoparticles causes difficulties, and only nanoscale can dramatically change physical properties [1–3]. Physical properties of nanocomposites are greatly influenced by the size scale of their components and the degree of mixing between the two phases. Depending on the method of preparation, the nature of the polymer matrix and of the nanofillers, composites significantly differing in properties can be obtained [3]. Properties of polymer-

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clay nanocomposites depend on the interaction mechanism between the polymer and clay. The differences in interaction between these phases result from the polarity, molecular weight, hydrophobicity, reactive groups, etc. of the polymer, the type of solvent, and the clay mineral type.

Various techniques of characterisation have been used in polymer research [2]. The commonly used techniques are scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), wide-angle X-ray diffraction (WAXD), and small-angle X-ray diffraction (SAXS) [3]. AFM and SEM are also required to characterize nanoparticle dispersion or distribution.

Imaging has already become a universal tool in many areas of science and engineering. Usually only the results of the qualitative analysis of microscopic observations are published, a quantitative image analysis of nanocomposite structure being rarely performed.

The paper presents the application of quantitative image analysis to describe morphological properties of boehmite and its nanocomposites. Nanosized ceramics, highly dispersed into polymer matrix materials, are widely investigated in terms of modification of polymer properties. The addition of ceramics with primary particle sizes of several nanometres allows specific tailoring of relevant thermal properties, e.g. lowering of the peak heat release rates (PHRR). The aim of our activities is to produce improvements in the fire performance of polyurethane. The nanocomposites were composed of polymers and organically modified boehmite. Boehmite is laminar aluminum oxyhydroxide with generalized formula AlO(OH) and is used as a flame retardant. It was modified with dibuthyl phosphate. Modification with dibuthyl phosphate causes changes of size and shapes of the boehmite grain. The combination of phosphate and clays in polyurethanes for higher flame retardant effects was studied.

In this paper, the influence of the quantity of boehmite and the size of agglomerate on the thermal and mechanical properties is presented.

2. Experimental

Materials. Dibutyl phosphate was supplied by Aldrich. Boehmite was modified by reaction with dibutyl phosphate for 1 h by the reported procedure [4]. Components used for PU synthesis were: poly(ethylene adipate) (PEA) mol. wt. 2000 Alfaster T620 (Alfa Systems), 4,4′diphenylmethane diisocyanate (MDI), Isonate M 125 (Dow Chemical), glycol (G1) and glycerine (G2) – G1, G2 (POCH).

Preparation of polyurethane/boehmite composite. Polyurethane nanocomposite matrices with the PEA:MDI:G1:G2 molar ratio of 6:9:2:1 were synthesized. Boehmite was added to the PU matrix in 0.5, 1.5, and 3.5 wt. % (Table 1). All samples were synthesized by a one-step method in *in situ* polymerization. Samples were formed by casting. The curing reaction was performed at 120 ºC for 16 h. Samples were aged at

room temperature for 14 days. Determination of the density of polyurethane and nanocomposites was performed according to ISO 2781.

SEM observations. The microstructure of nanocomposites was investigated on microsection and fracture surfaces. The fracture surface was obtained by breaking at liquid nitrogen temperature (–196 ºC). Then the samples were coated with a thin film of carbon. The morphology of boehmites and nanocomposites was characterized by high resolution scanning electron microscopy (HRSEM) LEO 1530.

Image analyses. Surface images were subject to graphic treatment by manual detection of particle contours. The obtained contour was transferred to the MicroMeter program, a quantitative analysis was performed and the equivalent diameter (d_2) of the agglomerate was calculated [5]. Measurements were performed for at least 200 agglomerates.

AFM observations. AFM topographic images were obtained using a Multimode Nanoscope IIIa (Digital Instrument INC., USA) working in a tapping mode. Nanocomposite samples were microtomed at –10 ºC using a glass knife with microtome Leica RM 2165 with system LN 21.

Thermal analyses. The properties of the fire reaction were investigated using a cone calorimeter according to the standard method prescribed in ISO 5660 at the heat flux equal to 50 kW/m^2. The nanocomposite samples 100×100 mm^2 in size and 4 mm thick were held in retaining frames protecting the specimen edges during testing. Each experiment was repeated three times. Peak heat release rate (PHRR), total heat release (THR), average specific extinction area (SEA), and time-to-ignition (t_{ig}) have been measured.

Mechanical properties. A tensile test was performed using an Instron 1115 tensile tester. The samples were elongated at the rate of 500 mm/min according to ISO 527. Hardness was measured using an indentation hardness tester according to ASTM D2240-75, abrasive wear was measured according to ISO 4649.

3. Results and discussion

Particles of modified boehmite form agglomerates. Modification with tributyl phosphate causes changes of size and shapes of boehmite grains (Fig. 1). The boehmite structure changes after the modification, and the particles form oval and fibre grains (Fig. 1). The modification caused the reduction of specific area of powders from 209.7 m^2/g for unmodified boehmite to 39.9 m^2/g for modified tributyl phosphate boehmite.

The microstructure of nanocomposites was investigated on the fracture surface; exemplary SEM images are presented in Fig. 2. Figure 3 presents binary images on the fracture surface of boehmite agglomerates in the polyurethane matrix.

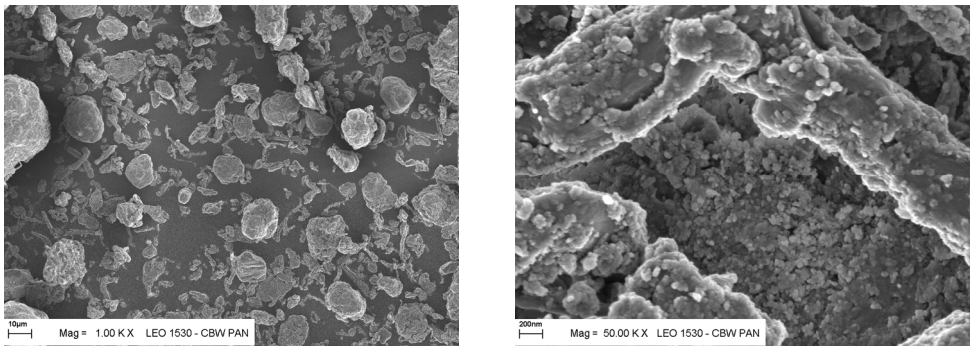

Fig. 1. SEM images of modified boehmite: agglomerate (left), structure of agglomerate (right)

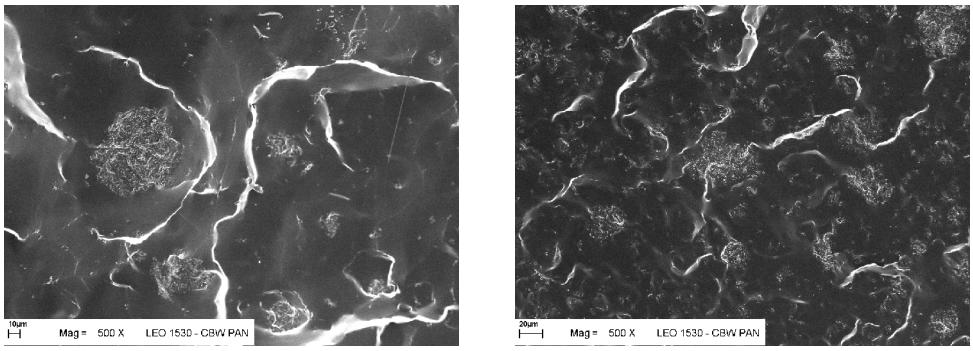

Fig. 2. SEM images of the fracture surfaces of nanocomposites
with modified boehmite: 1.5 wt. % (left) and 3.5 wt.% (right)

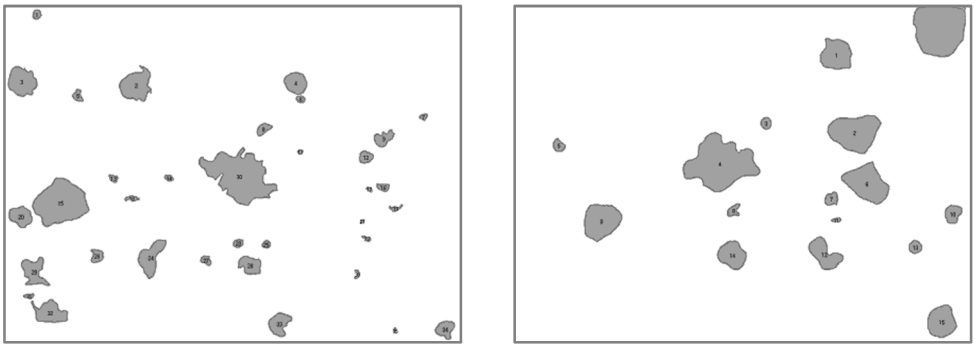

Fig. 3. Binary images of agglomerates of modified boehmite
in the polyurethane matrix: 1.5 wt. % (left) and 3.5 wt.% (right) of boehmite

The results of the analysis of the sizes of boehmite agglomerates in the polyurethane matrix are given in Table 1.

Table 1. Sample identification and composition

Identification	Composition	Size of agglomerate, d_2 [μm]
PU/B1	polyurethane + modified boehmite 0.5 wt. %	16.7 ± 9.2
PU/B2	polyurethane + modified boehmite 1.5 wt. %	23.2±12.7
PU/B3	polyurethane + modified boehmite 3.5 wt %	26.1±14.4
PU/BN	polyurethane + unmodified boehmite 3.5 wt %	38.5±13.6

Figure 4 shows time dependences of the heat release rate (HRR) for polyurethane and a nanocomposite with 3.5 wt. % of modified boehmite. In the case of the nanocomposite, lower peak heat release rates (PHRR) were always combined with a reduction of the time to ignition (from 48 s for PU to 29 s for nanocomposites). Average smoke density did not change.

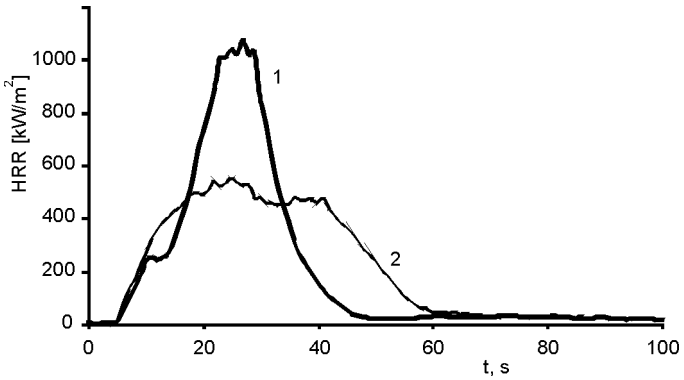

Fig. 4. Heat release rate curves for samples of polyurethane (1) and polyurethane with 3.5% of modified boehmite (2)

Table 2. Selected physico-mechanical properties of the samples

Sample	Density [g/cm^3]	Tensile strength [MPa]	Elongation at break [%]	Tension set [%]	Abrasive wear [cm^3]
PU	1,2274	39,4	500	2,1	24,4
PU/B1	1,2341	17,6	605	4,6	32,9
PU/B2	1,2385	22,1	660	6,8	32,9
PU/B3	1,2433	25,8	580	7,5	31,4
PU/BN	1,2456	42,6	580	4,4	64,3

The tensile strength of nanocomposites with modified boehmite is lower than that of neat polyurethane (Table 2). Addition of unmodified boehmite causes a double increase of the abrasive wear, and addition of modified boehmite causes an increase of the abrasive wear of about 10% (Table 2).

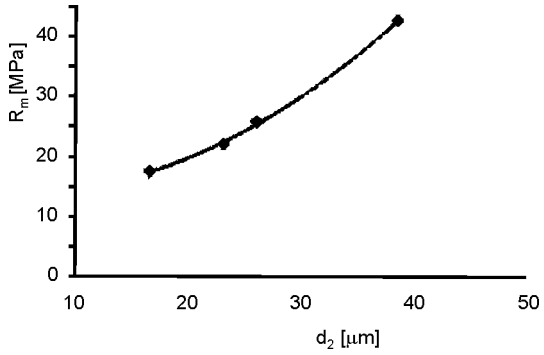

Fig. 5. Dependence of the tensile strength on the diameter of the agglomerate

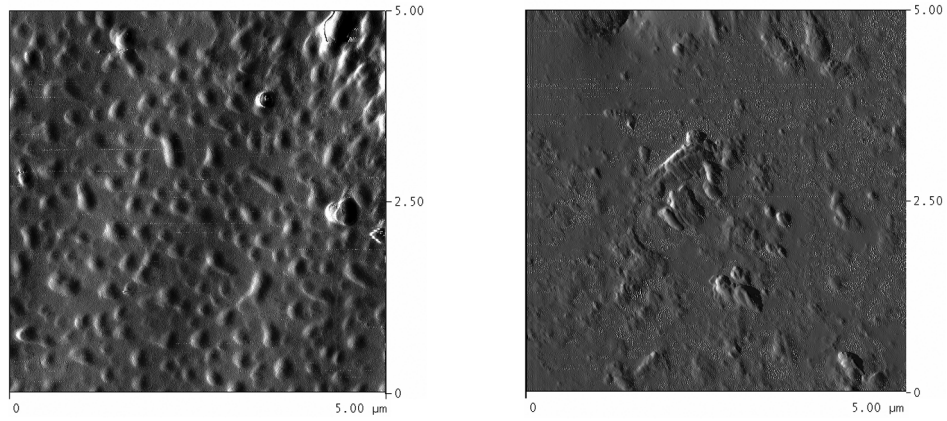

Fig. 6. AFM images of the surface of the cross sections of nanocomposites with 0.5 wt. % (left) and 1.5 wt. % of modified boehmite

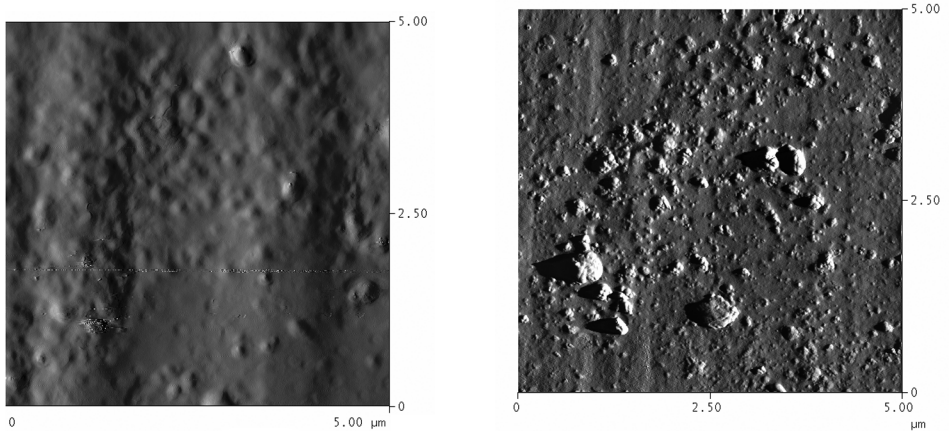

Fig. 7. AFM images of the surfaces of the cross sections of nanocomposites with 3.5 wt. % of modified boehmite (left) and unmodified boehmite (right)

It can be expected that the nanoparticle homogeneous dispersion will not change the value of the nanocomposite abrasive wear. To explain the reason for the lower tensile strength of nanocomposites with boehmite, the dependence of the tensile strength on the diameter of an agglomerate was analysed, and the results are shown in Fig. 5. It was found that the tensile strength increases with the increasing diameter of the agglomerate of boehmite.

Physical properties of nanocomposites depend on properties of polymer matrices. The change of the elongation at break and tension set could suggest that during synthesis the domain structure of polyurethane matrix changes. This observation was confirmed by the AFM image analysis (the surface was scanned between agglomerates of boehmite) (Fig. 6, 7) and the density measurements (Table 2). Phosphate compounds influence the reaction kinetics of polyurethane substrates, and this may cause formation of the polyurethane domain structure.

4. Conclusion

Boehmite modified with tributyl phosphate reduced the peak heat release rates of polyurethane nanocomposites but also reduced the time to ignition. A better dispersion in the polymer matrix is necessary for optimizing this potentially new class of fire retardant additives. The results show that boehmite based nanocomposites may be used for the preparation of halogen-free and environmentally friendly flame retardant polyurethane materials. The change in polymerization of polyurethane matrix needs to be explained by further research.

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