TECHNICAL TRANSACTIONS | **CZASOPISMO TECHNICZNE**
CHEMISTRY | CHEMIA
1-Ch/2014

TEODORA SIKORA*, KRYSTYNA WIECZOREK-CIUROWA*

PROSPECTS OF USING MECHANOCHEMICAL SYNTHESES IN THE FABRICATION OF COMPOSITE POWDERS FOR TRIBOTECHNOLOGY

PERSPEKTYWY UŻYCIA SYNTEZ MECHANOCHEMICZNYCH DO WYTWARZANIA PROSZKÓW KOMPOZYTOWYCH DLA TRIBOTECHNOLOGII

Abstract

The aim of tribotechnological research is the reduction of tribo-couple wear through the optimization of the functional properties of the materials. Polymer matrix composites enriched by powdered materials (e.g. metal-ceramic composite powders) have a wide range of applications in the field of tribotechnology. The possibilities of producing such fillers via green, environmentally-friendly syntheses using the high-energy ball milling process are presented.

Keywords: *mechanochemistry*, *frictional materials*, *tribology*, *composite powders*

Streszczenie

Optymalizacja właściwości użytkowych w oparciu o ograniczenie zużycia powierzchni par trących jest przedmiotem badań tribotechnologii. Szerokie zastosowanie w tej dziedzinie znajdują materiały kompozytowe z osnową polimerową, uszlachetniane materiałem proszkowym, m.in. proszkami kompozytowymi metaliczno-ceramicznymi. Przestawiono możliwości wytwarzania takich napełniaczy na drodze ekologicznych syntez z użyciem wysokoenergetycznego procesu mielenia.

Słowa kluczowe: *mechanochemia*, *materiały cierne*, *tribologia*, *proszki kompozytowe*

---

* Ph.D. Student Eng. Teodora Sikora, Prof. Ph.D. D.Sc. Krystyna Wieczorek-Ciurowa, Faculty of Chemical Engineering and Technology, Cracow University of Technology.

1. Introduction

In ancient times, mankind tried to improve the strength and mechanical properties of functional materials. Around 800 BC, bricks made in the Near East were reinforced with straw and then sun-dried – as a consequence, they were stronger and were more compression resistant than fired bricks. This was the first step towards composite materials engineering. Composites are defined as materials composed of at least two different components, i.e. the matrix and the filler. The specific properties of the composite are greater than the sum of its parts. The new materials show specific, advanced mechanical and chemical features due to synergy of the components' properties.

The intensive development of materials engineering at the beginning of the 20th century caused a growing interest in new methods of composite materials production. Simultaneously, pro-ecological, environmentally friendly methods of materials production became increasingly desired. One of these methods, mechanochemical synthesis, has been in use since the 1960s. Based on the changing of mechanical energy to chemical energy, it allows for the obtaining of functional materials such as alloys, intermetallics, composite powders, catalytic precursors and ceramics with a wide range of properties (e.g. perovskite ceramics) [1]. The application of mechanochemically synthesized ceramic-ceramic and ceramic-metallic powders as fillers of polymer matrix composites (PMCs) could improve the properties of functional materials and lower the costs of their production.

Nowadays, the automotive and machinery industries are important consumers of composite materials. Polymer composites with particulate reinforcement are known to have high values of wear resistance and hardness. These properties can be tailored to the specific field of application. For this reason, complex functional materials are the most commonly used components for tribo-elements [2, 3].

The main object of tribology is the investigation of phenomena observed in the contact of solids. These macro and micro-interactions between two mating surfaces have a crucial influence on the tribological characteristics of the material. Furthermore, tribology deals with practical issues relating to wear factors of tribo-couple surfaces. The creation of reasonable and useful tribological systems based on the requirements defined by tribology is an objective of tribotechnological investigation. In other words, tribotechnology is involved in developing practical applications of tribology. Mainly, it is focused on the optimization (increasing or decreasing) of the friction coefficient in the friction node and on wear decreasing technologies.

Mechanochemical synthesis is a relatively new technology of powders production. The powdered materials can be used as fillers of polymeric matrix to form the elements of frictional couples. This explains why mechanochemical synthesis can be a new approach for tribotechnology.

2. Composite materials for tribotechnology

The term 'composites' defines a wide group of materials differing in their physicochemical properties, composition or structure. Composites are classified into numerous groups by their origin, type of reinforcement, application or type of matrix. Different materials are applied as the matrix: metals (MCMs – Metal Matrix Composites); ceramics (CMCs – Ceramic Matrix Composites); polymers (PMCs – Polymer Matrix Composites) [4].

The PMCs are the specific group of materials for tribological applications. Such materials are widely used in the automotive industry as components of braking systems, bearings, clutches, etc. The polymeric matrix decreases the mass of tribo-elements and increases their corrosion resistance, vibration damping capacity and ease of shaping. However, the disadvantages of polymer matrices are their increased thermal expansion, swelling in contact with lubricants and lower thermal conductivity. Therefore, modification of polymer properties to counteract these disadvantages by using various fillers is required.

The wear resistance is the primary factor which determines the usefulness of composites in tribology. It is documented that wear performance can be markedly improved by using a composite filler or various combinations of fillers. This modification of adding fillers may considerably extend the service life of composites. This parameter depends on the filler type, volume fraction and its distribution within the matrix.

The type of filler has a critical effect on the properties of composites and its application. Using powdered reinforcement is the most commonly applied means of increasing its mechanical strength [5]. However, the improvement of mechanical properties not only depends on the filler type, but also on the size and shape of reinforced particles. Numerous papers report on the straight influence of the above-mentioned parameters on electrical and thermal conductivity, thermal resistance [6], mechanical strength, flammability and optical properties of composites [7]. Composites filled with smaller particles present higher levels hardness and stiffness [8], thus meeting the basic requirements of materials for the automotive industry [9].

3. Manufacturing of the composite fillers

Tribological systems (tribo-couples) filled with particles consist of strengthening components (mica, silica, basalt tuff) and modifiers of properties (inorganic compounds, composite powders). The proper selection of modifiers depends on the intended use of the material. Modifiers such as Al_2O_3, SiO_2, SiC, ZnO, ZrO_2 and Fe_3O_4 increase and stabilize the friction coefficient. Particles of MoS_2, ZnS, CuS and graphite are used as lubricants to reduce friction and wear [10]. Tailoring the type and filling ratio of friction modifiers allows for the obtaining of a material that displays excellent wear and friction characteristics.

Powdered fillers can be produced by a variety of traditional techniques, such as sol-gel, impregnation, reduction [11], plasma process [12] or, alternatively, by means of mechanochemical synthesis. The essence of mechanochemical synthesis is the manufacturing of new materials via solid-state reactions induced by high-energy milling. The mechanical energy is introduced and accumulated in the milled material in the form of stress and lattice defects. These phenomena promote the creation of new systems and compounds. Mechanochemical synthesis is a one-step process, thus, the manufacturing of composites is easier and faster. Additionally, the method generates virtually no waste and does not require the application of solvents. Mechanical synthesis is an universal and useful method because it offers flexibility in the selection of substrates, the reactions are carried out in the solid-state. Therefore, the application of mechanical synthesis for the production of metallic-ceramic and ceramic-ceramic powders is gaining ground as an interesting alternative to traditional routes for the manufacturing of composite fillers.

4. Composite powders – selection of the best polymer matrix fillers

The applicability of composite powders as fillers of the polymer matrix mainly depends on the particle shape, size, size distribution and chemical homogeneity.

The mean size of the filler particles is a crucial parameter of the composite material properties**.** The term *nanocomposites* is applied to polymers filled with nanoparticles (an average particle size of 10–100 nm). In microcomposites, particles with a diameter higher than 100 nm are used.

The shape of the filler particles is a supplementary parameter of reinforcement characterization. The classical theory of manufacturing ceramic powders indicates that a spherical shape is most convenient for sintering. However, for some applications, spherical powders show unsatisfactory properties. For example, platelet-shaped particles of ferrites (e.g. $BaFe_{12}O_{19}$) show better magnetic properties [13]. A wide-range of applications is also observed for composites filled with SiC whiskers. These acicular particles significantly improve fracture toughness of the material.

Particle size distribution is the key parameter in functional materials. Most of the ceramic materials require a narrow size distribution, especially when the manufactured material is intended for consolidation by sintering.

Producing monodisperse powders is as unfavorable as manufacturing material with a wide particle size distribution. These types of powders tend to form dense geometric packing areas joined with groups of loosely coupled grains. The described phenomena are unfavorable during sintering processes and cause the formation of wide pores in the sintered material. Moreover, monodisperse powder is prone to create mechanically stable agglomerates. The slightest differentiation of grain size can be obtained by 'wet' methods of particle manufacturing (e.g. sol-gel or precipitation methods). Methods based on the grinding of materials allow for the production of powdered material with diverse grain sizes. These powders tend to mechanical densification (hot pressing) and sintering.

Filler distribution in the matrix – in most cases, the homogeneous distribution of filler particles in the matrix is of paramount importance with respect to the intended tribological applications. The technology of composite manufacturing (including the method of matrix-reinforcement homogenization) depends on the type of manufactured composite and component properties (e.g. type of polymer matrix).

Functionally graded materials (FGMs) are a group of very special engineering composites. These materials have a graded composition and show the variation of properties as a function of the place where these parameters are measured. In other words, FGMs are the composites wherein the filler-matrix volume ratio or type of the reinforcement change along the defined direction. Nowadays, functionally graded structures are increasingly applied in numerous engineering systems including sensors, electronics, magnetic components, machine parts and many others [8, 14]. FGMs are applied everywhere where smoothly changing properties are desired and cannot be realised in uniform materials. For example, the material structure may possess a smooth transition from hard phases (with good sliding properties on the one side), to a structure with high toughness and thermal conductivity on the other (inner) side. With their gradual variation in composition, FGMs may exhibit good resistance to wear and thermal stress and hence, are readily applied for sliding bearings and rollers [8].

5. Effects of the fillers on the mechanical properties of PMCs

Erosion of the contact sides is a serious problem in engineering systems. This phenomenon involves the progressive loss of material and generates high costs with regard to industrial processes. It is well-known that the erosion rate of the polymer composites is higher than that of the neat polymers [15]. Erosion refers to the gradual wear of tribo-couple surfaces through the repeated impact of small solid particles which are the wear products of tribo-couple cooperation. Especially the coarse particles being accelerated to the very high velocities in a gas or liquid carrier, entrapped between the contacting surfaces may lead to serious degradation of both sliding-pair components. Except for erosion, additional unwanted processes such as thermal, chemical and physical reactions take place in the friction zone [16, 17].

Depending on the particle impingement angle, two different erosive wear mechanisms are proposed - ductile erosion and brittle erosion. In ductile erosion, the maximum material removal occurs at impingement angles (α) lying between 15 and 30°. Brittle erosion is observed at $\alpha \approx 90°$. In PMCs, the maximum wear rate is observed for α ranging from 45 to 60°, therefore, the erosion mechanism is defined as *semi-ductile* [18, 19].

When discussing the erosion rate of PMCs, it is necessary to consider a few important factors including:

- the type of polymer matrix (thermosetting or thermoplastic),
- the type of filler material (fibers or particles) and its characteristics (brittleness, hardness, length and aspect ratio, orientation in the matrix, etc.),
- the volume fraction of fillers.

It has been proven that particulate fillers can be successfully used as erosive wear modifiers [20, 21]. Composites filled with very hard particles (e.g. Al_2O_3) show better erosion resistance than materials filled with softer particles (e.g. the mixture of SiC and fly ash). The reduction in material loss can be explained by two reasons. Firstly, the bulk hardness of composite increases when hard particles are applied. Secondly, a high amount of the erodent energy can be absorbed by other particulate fillers, thus decreasing the energy absorbed by the matrix and, optionally, fibers [16]. The synergistic effect of those phenomena markedly decreases the rate of erosion and consequently, increases the service life of the interacting elements.

The study is partially supported by the Polish Ministry of Science and Higher Education, projects C-1/KWC/DS/2013-14 and C-1/DS-M/2013-14.

References

[1] Wieczorek-Ciurowa K., *Mechanochemical Synthesis of Metallic-Ceramic Composite Powders*, R. Banerjee, I. Manna (Eds.), *Ceramic Nanocomposite*, Woodhead Publ. Ltd, Abington Hall, Great Abington Cambridge, UK, 2010.

[2] Friedrich K., Chang L., Haupert F., *Current and Future Applications of Polymer Composites in the Field of Tribology* [in] Nicolais L., Meo M., Milella E. (Eds.), *Composite Materials: A Vision for the Future*, Springer-Verlag London Ltd, London, UK, 2011.

[3] Zhang Z., Friedrich K., *Tribological characteristics of Micro- and Nanoparticle Filled Polymer Composites* [in] Friedrich K., Fakirov S., Zhang Z. (Eds.), *Polymer Composites. From Nano- to Macro-Scale*, Springer Science+Business Media, Inc., 2005.

[4] Basu B., Kalin M., *Tribology of Ceramics and Composites. A Materials Science Perspective*, Ch. 2, John Wiley & Sons, Inc., 2011, 7-17.

[5] Friedrich K., Chang L., Haupert F., *Current and Future Applications of Polymer Composites in the Field of Tribology* [in] Nicolais L., Meo M., Milella E. (Eds.), *Composite Materials. A Vision for the Future*, Springer-Verlag London Ltd., 2011, 127-167.

[6] Nikkeshi S., Kudo M., Masuko T., *Dynamic Viscoelastic Properties and Thermal Properties of Ni Powder-Epoxy Resin Composites*, Journal of Applied Polymer Science, vol. 69, 1998, 2593-2598.

[7] Hanemann T., Vinga-Szabo D., *Polymer-Nanoparticle Composites: From Synthesis to Modern Applications*, Materials, vol. 3, 2010, 3468-3517.

[8] Friedrich K., Zhang Z., Schlarb A. K., *Effects of Various Fillers on the Sliding Wear of Polymer Composites*, Composites Science and Technology, vol. 65, 2005, 2329-2343.

[9] Garces J.M., Moll D.J., Bicerano J., Fibiger R., McLeod D.G., *Polymeric Nanocomposites for Automotive Applications*, Advanced Materials, vol. 12, 2000, 1835-1839.

[10] Bahadur S., Schwartz C., *Mechanical and Tribological Behaviour of Polymers Filled with Inorganic Particulate Fillers* [in] Sinha S.K., Briscoe B.J. (Eds.), *Polymer Tribology*, Imperial College Press, London 2009, 416-448.

[11] Hussain F., Hojjati M.I., Okamoto M., Gorga R.E., *Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview*, Journal of Composite Materials, vol. 40, 2006, 1511-1575.

[12] Vollath D., *Plasma Synthesis of Nanopowders*, Journal of Nanoparticle Research, vol. 10, 2008, 39-57.

[13] Haberko K., *Proszki Ceramiczne – Budowa i Wymagania*, Inżynieria Materiałowa, vol. 2 (85), 1995, 35-41.

[14] Lee N.J., Jang J., Park M., Choe C.R., *Characterization of Functionally Gradient Epoxy/Carbon Fibre Composite Prepared under Centrifugal Force*, Journal of Materials Science, vol. 32, 1997, 2013-2020.

[15] Arjula S., Harsha A.P., *Study of Erosion Efficiency of Polymers and Polymer Composites*, Polymer Testing, vol. 25, 2006, 188-196.

[16] Płaza S., Margielewski L., Celichowski G., *Wstęp do tribologii i tribochemia*, Wydawnictwo Uniwersytetu Łódzkiego, Łódź 2005.

[17] Patnaik A., Satapathy A., Chand N., Barkoula N.M., Biswas S., *Solid Particle Erosion Wear Characteristics of Fiber and Particulate Filled Polymer Composites: A review*, Wear, vol. 268, 2010, 249-263.

[18] Barkoula N.M., Karger-Kocsis J., *Review. Processes and Influencing Parameters of the Solid Particle Erosion of Polymers and their Composites*, Journal of Material Science, vol. 37, 2002, 3807-3820.

[19] Chowdhury A.A., Nuruzzaman D.M., Rahaman M.L., *Erosive Wear Behaviour of Composite and Polymer Materials – A review*, Recent Patents on Mechanical Engineering, vol. 2, 2009, 144-153.

[20] Patnaik A., Satapathy A., Mahapatra S.S., Dash R.R., *Implementation of Taguchi Design for Erosion of Fiber Reinforced Polyester Composite Systems with SiC Filler*, Journal of Reinforced Plastics and Composites, vol. 27, 10, 2008, 1093-1111.

[21] Patnaik A., Satapathy A., Mahapatra S.S., Dash R.R., *Tribo-performance of Polyester Hybrid Composites: Damage Assessment and Parameter Optimization Using Taguchi Design*, Materials and Design, vol. 30, 2009, 57-67.