

The Synthesis of Nanocomposites with Use of Cellulose

G.K. Maylieva¹, A.A. Mirzaev^{1*}, G.E. Satayeva¹,
J. Jandosov², Z.A. Mansurov²

¹The South Kazakhstan State University named after M.O. Auezov,
5 Tauke khan St., Shymkent, Kazakhstan

²The Institute of Combustion Problems, 172 Bogenbay Batyr St., 050012,
Almaty, Kazakhstan

Abstract

This work studied the synthesis of nanocomposites with cellulose use as crystallizing polymer on the basis of its ability to form crystalline particles with various parameters of an elementary cell – nanoparticles of a metal or oxide origin.

The authors obtained high dispersed systems by dispersion of volume phases from solutions using condensation method. At using of this method, depending on the conditions of the formation process of the new phase can be obtained as systems with a size of several nanometers as well as more coarsely dispersed systems. The dispersiveness of a system, arising during formation of new phases, is determined by ratio speed of formation and nucleus growth of new phase a phase transition. The condensation process involves the formation of new phase according the heterogeneous or homogeneous mechanisms. The kinetics formation of new phase is determined by two stages: the formation of condensation centers (nucleus) and nucleus growth.

In formation process of nanocomposite materials the natural polymer with known molecular structure is used as matrix, in which we can put desired nanoparticles in the form of filler. In this work the authors used cellulose which has developed capillary-porous structure, including in-fibrillar porous with the size of 1,5-10 nm, and which is able to form crystallites with different parameters of lattice cell.

Introduction

At the present time the nanosized powders of ceramic materials are widely used in industry. In contrast to the ceramic nanopowders, metalpowder market is just being formed, and while its volume is relatively small. Dispersion and condensation are routine methods for obtaining of free dispersion systems – powders, suspensions, sols. Under dispersion we can understand the granulation and pounding, and under condensation – the formation of heterogeneous dispersion system from homogeneous as the result of molecular association, atoms or ions. Thus, high dispersed systems can be obtained either by dispersion of volume phases, or at separation of disperse particles from solutions or one-component homogeneous systems (condensation formation of dispersion systems).

Materials and Methods

At using of the condensation methods, depending on the conditions of the formation process of the new phase can be obtained as systems with a size of several nanometers as well as more coarsely dispersed systems, and also monocrystalline samples with big sizes (tens of centimeters) ideal to the structure. The dispersiveness of a system, arising during formation of new phases, is determined by ratio speed of formation and nucleus growth of new phase a phase transition.

The condensation process involves the formation of new phase according the heterogeneous mechanism on existing condensation nuclei (ions, particles of foreign substances) or homogeneous, on the surface of nucleus, arising spontaneously as the result of density fluctuations of the matter in the system.

*corresponding author. E-mail: aibek.mirzaev@mail.ru

At homogeneous condensation the certain critical degree of repletion of stream is corresponding to the inception of condensation centers, depending on the nature of substance. Self-existing formation of nucleus is occur, the surface energy act as potential barrier of condensation.

The kinetics formation of new phase is determined by two stages: the formation of condensation centers (nucleus) and nucleus growth. Nucleation rate of condensation centers and their further growth is determined by the fluctuation theory with probability of formation of this center. Fundamentals of kinetic theory of nucleus formation of a new phase were in work of M. Volmer and further developed in works of Frenkel and others.

The ratio of nucleation rates of condensation and their rate determines not only the particle radius, but also their size distribution. As usual we get dispersion systems with wide size distribution. The particle size is determined by concentration gradient. At that there are two extreme cases of particle size limit: the diffusion kickout mechanism is associated with input of the matter to the particle surface and the kinetic – with transmission of molecules from vapor to the surface, it means with interaction of molecules at the surface. If nucleation rate of new phase is large enough, and their growth is slow, then the system with a large number of small particles is formed, of course under conditions that prevent their adhesion (coagulation). At small nucleation rate and their quick growth the dispersion system with small number of large particles is formed.

Thus, the problems that confronted the researcher or engineers to obtain corresponding dispersed systems with desired properties (particle size) dictate the synthesis process with corresponding control parameters of both stages of particle formation. Most often control the temperature, at which the synthesis of dispersion phase is conduct.

Results and Discussion

The reduction of particle sizes of solid body low of some threshold leads to substantial modification of their characteristics. Threshold size of particles at that the dimensional effect begins to operate jump-like for most presently known materials is varied from 1 to 100 nm. This is due to the fact that lengths, on which the basic physical strengths in substance appear, and varies in a range from 1 to 100 nm.

The dependence of physical-chemical properties from particle size is considered according the ex-

ample of optical spectrum [1], magnetic properties [2, 3], thermodynamics [4], electro-chemistry [5], electrol conductivity and electron transfer [2, 6].

Different equations, describing the dependence of physical properties from particle size, are given in [7].

According the X-ray and electron diffraction results, the particle size which shows the crystalline properties, is 3-5 nm, the other physical investigation methods – 1-10 nm. Typically, aggregations containing from two to several hundred atoms, are called clusters, and larger aggregations (with a diameter 0,1 nm) called as particles. A distinctive feature of clusters is the absence of definite crystalline structure and the deviation of substance composition from stoichiometry. Some researchers believe that lower orientation dimensional bound of nanoparticles D_{min} is about 1 nm. Lower bound is approximately localized in $7d_a < D_{min} < 10d_a$, where d_a – atom diameter.

If the particle size closer to D_{min} , so the dependence of different properties from particle size will effect stronger.

The kinetic of chemical interaction of nanoparticles has a character of molecular reaction. The developed surface of nanoparticles leads to the thermodynamical effects, related to their size. A well-known Tompson's formula predicts the temperature drop of particle melting, inversely proportional to their radios. Experimental reduction of melting temperature for 20-30% observed in the particles, the size of which approximately less than 10 nm.

The transmission from massive crystalline body to the nanoparticles is accompanied by change of interatomic distance and parameters of crystalline lattice. The most likely reason for the reduction of the lattice constant of nanoparticles is underbalance of interatomic bound of surface atoms in contrast to atoms located in the volume of the particle.

So in formation process of nanocomposite materials the natural polymer with known molecular structure could be used as matrix, in which we can put desired nanoparticles in the form of filler. For this role the activated lignocellulose is most appropriate. The cellulose can be activated by phosphorous or nitric acids, then the chemical transformations occurring in macromolecule of cellulose affect on its ion-exchange properties and biological activity. At that the structure-modified cellulose, which has a significantly greater (in 2.5 times) sorption capacity to inorganic salts is formed. Further, during impregnation by activated lignocellu-

lose the aqueous solution of salt, which has ions of desired metals in essential stoichiometrically relations for synthesis and heat treatment the nanocomposite material is formed.

Here, the cellulose fibers act as reinforcing bearer in relation to salt components and prevents their aggregation during heat treatment. At the same time, the cellulose matrix act as dispergator which is

formed graphite, which represents loose flakes (Fig. 1) preserving the origin texture of the fragments of cellulosic materials and dispersing to the powder with particle size 10 nm, which were grouped in such a way that follows the shape of cellulose fibers – matrix, on which the nucleus formation and particle size is occurred. See Table 1 and Fig. 2.

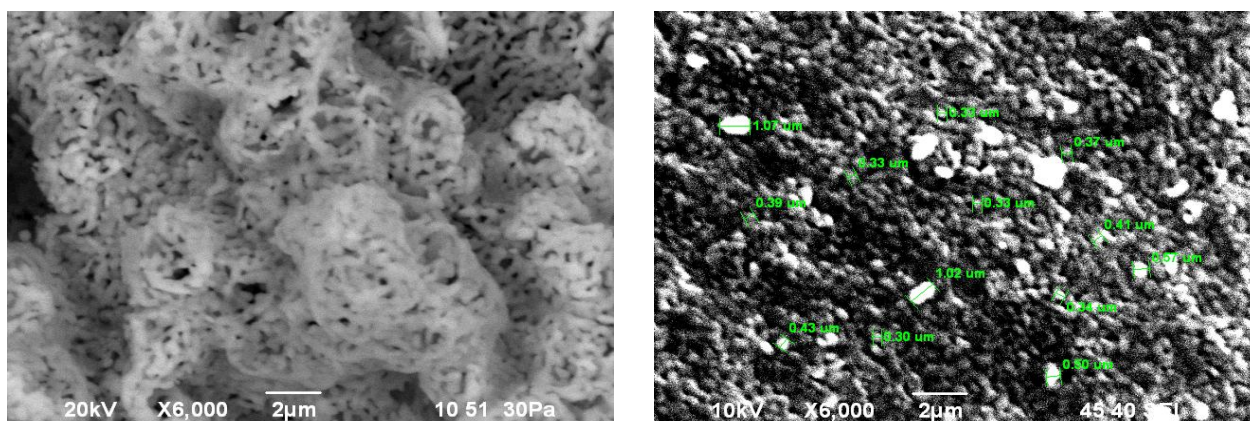


Fig. 1. Electron microscopic image of composite is obtained with using of cellulose material.

Table1

Element content of the composite obtained using cellulose material

Element	Al	Si	Ca	Mn	Fe
Wt %	0.45	0.15	0.44	0.06	75.73

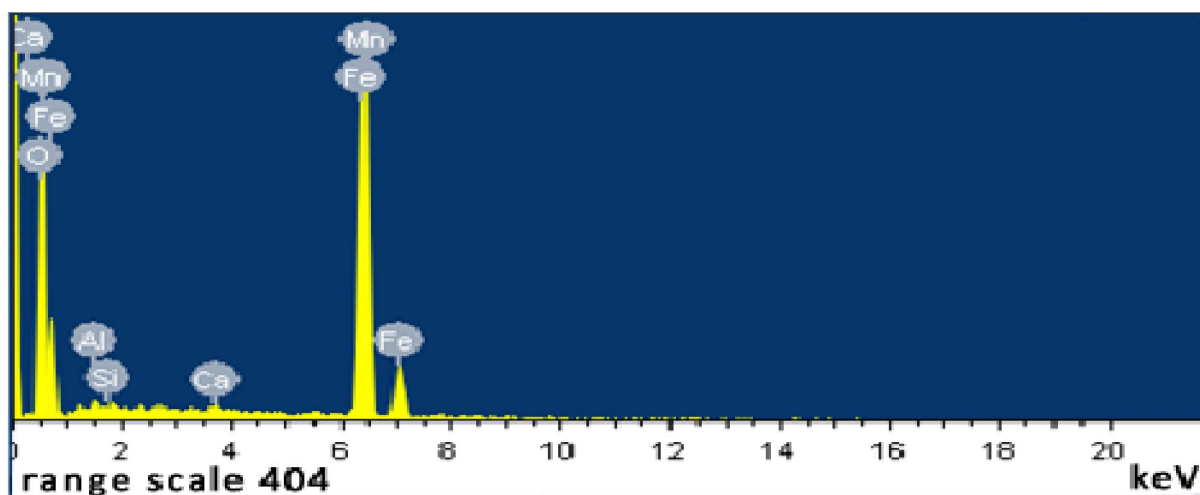


Fig. 2. Ultimate composition of composite according the EM data.

Conclusions

Thus, the use of cellulose which has developed capillary-porous structure, including in-fibrillar porous with the size of 1.5-10 nm, as well as channels and microporous in fibers of natural cellulose with the diameter of several micrometers are respon-

ble for the flow not only absorption, but also capillary intake. Therefore, for cellulose as crystallizing polymer the effect of polymorphism is typically, it means that the ability to form crystallites with different parameters of lattice cell – nanoparticles of metallic or oxide origin. At that the cellulose as matrix gives the possibility to form composite.

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