SILICA HYBRID PARTICLES SYNTHESIZED THROUGH SOL-GEL PROCESSES

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Se studiază prepararea particulelor hibride prin procesul sol-gel al tetraetoxisilanului (TEOS) împreună cu metacriloxipropil trietoxisilanul (MPTS). Dimensiunile particulelor variază între 50 şi 500 nm iar potenţialul Zeta între -20 şi -5 mV în funcţie de raportul dintre reactanţi. Dimensiunile particulelor şi potenţialul Zeta scad cu creşterea concentraţiei de MPTS din sistem. Acest lucru se explică prin interacţiile hidrofobe dintre parteneri şi trimetoxisilan.

Aqueous suspensions of hybrid particles have been prepared by means of a sol-gel process using the hydrolysis and condensation of tetraethoxysilane (TEOS) and methacryloxypropyltrimethoxysilane (MPTS). Depending on the reactants ratio, the particle sizes were found between 50 and 500 nm and the Zeta potential was varying between - 20 and - 5 mV . The particles dimensions and the Zeta Potential decreased with the increasing MPTS concentration from the system. This was explained through hydrophobic interactions between partners and trimethoxysilane.

Key words: hybrid, silica, sol-gel

1. Introduction

From the last 50 years, the nanocomposites material synthesis by embedding nanosized inorganic particles into polymers became a very interesting research domain. Herrera et all. reported the chemical modification of Laponite clay minerals using monofunctional γ - methacryloxy propyl dimethyl ethoxysilane and trifunctional γ – methacryloxy propyl trimethoxysilane

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molecules by using silane coupling agents, their aim being to produce colloidal nanocomposites with covalent grafting between the exfoliated clay sheets and the polymeric matrix [1].

For optimal control of the properties of these new materials, it is highly important to tailor the formation process from the point of view of the final product [2]. For example the formation of highly optical transparent material requires another process other than that of a system with good thermal and mechanical properties.

While in the most of the studies, tetraakoxysilanes were used as precursors for the inorganic network, trialkoxysilanes with an organic functionality have also been employed. The organic groups have often a significant influence on the resulting material. Kickelbick says that for a hybrid material formed from poly (VAc) and phenyltriethoxysilane, the glass transition temperature (Tg) of the polymer increases in a similar way as it does with TEOS as precursor [2].

A well known paper, referring at silica's particles synthesis, which is subsequently cite in the majority reviews is the one of Stöber and Fink (3). The sol-gel process of tetralcoxysilane in alcohol with C1-C4 chains through basic catalysis is the aim in this review. A very interesting phenomenon is that the silica's particles maximum diameter is synthesized at a 6 mol/L concentration of water in ethanol. Recent studies (4, 5) demonstrated that alcohol-water mixtures are nanostructured, and the alcoxysilanes solubilization does not destroy this autoagregation process. Sol-gel process realized in nonstructural systems is initially affected by the partners association in the apparently homogenous mixtures. Surfactants presence modifies the hydrophobic phase dimensions without destroying the nanostructure character of the initial systems (6, 7).

Our aim is to obtain silica's particles which contain polymerizable metacryloyl groups (8) of which concentration can be mould through ratio modification between metacryloyl propyltrimethoxysilane (MPTS) and tetraethoxysilane (TEOS) (9).

2. Experimental part

Materials: metacryloyl propyltrimethoxysilane (Fluka), tetraethoxysilane (Merck - Schuchardt) are used as such. Ethanol (Chimopar) was purified through rectification. Nonylphenol etoxilated with 25 moles ethylene oxide, technical product, was used as such. Polyethylenoxide methacrylate (MPEG2000) was synthesized as in (7).

Analysis

Particles dimensions were measured with a Nicomp 270 instrument.

Zeta Potential was measured with a Zetasizer Nano ZS (Malvern) instrument.

MPTS/TEOS silica's particle synthesis

The synthesis takes place at room temperature, in a glass reactor with magnetic stirrer (300 rot./min.). To a mixture of 8.7 cc EtOH with 1 cc MPTS/TEOS, 1.75 cc NH_4OH 25% are poured under stirring. After 30 minutes, the whole mixture is poured on 20 cc aqueous solution which contains 1% surfactant (MPEG200 or $NPEO_{25}$). The mixture is continuously stirred for 2 hours, after that, the aqueous mixture is analyzed.

3. Results and discussion

The synthesis was focused on the hybrid particles obtained from the mixture of MPTS/TEOS through sol-gel processes. Polyethylene glycol metacrylate (MPEG2000) was used as stabilizer, for a good interaction between the metacryloyl types of hydrophobic particles existing in the partner's molecules to be provided.

The synthesized particle medium diameter variations are shown in Fig.1. A strong decrease of the particles medium diameters with the increasing of MPTS concentration from the initial mixture is observed. Through the increase of metacryloyl groups, a good interaction with the surfactant is provided and a good stabilization of the hybrids particle as following. Particle dimensions distribution is relatively narrow. In the case of the ratio MPTS/TEOS = 50/50, a monomodal distribution was obtained (Fig. 2).

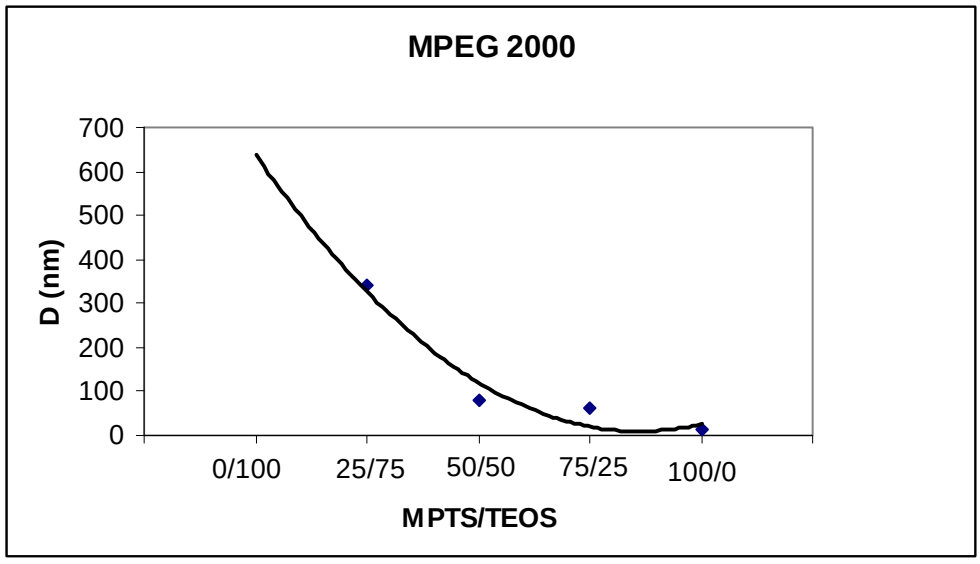

Fig.1 The decrease of medium diameter of hybrids particle obtained in the presence of MPEG2000, depending on the modification of the ratio MPTS/TEOS (MPTS/TEOS – g/g)

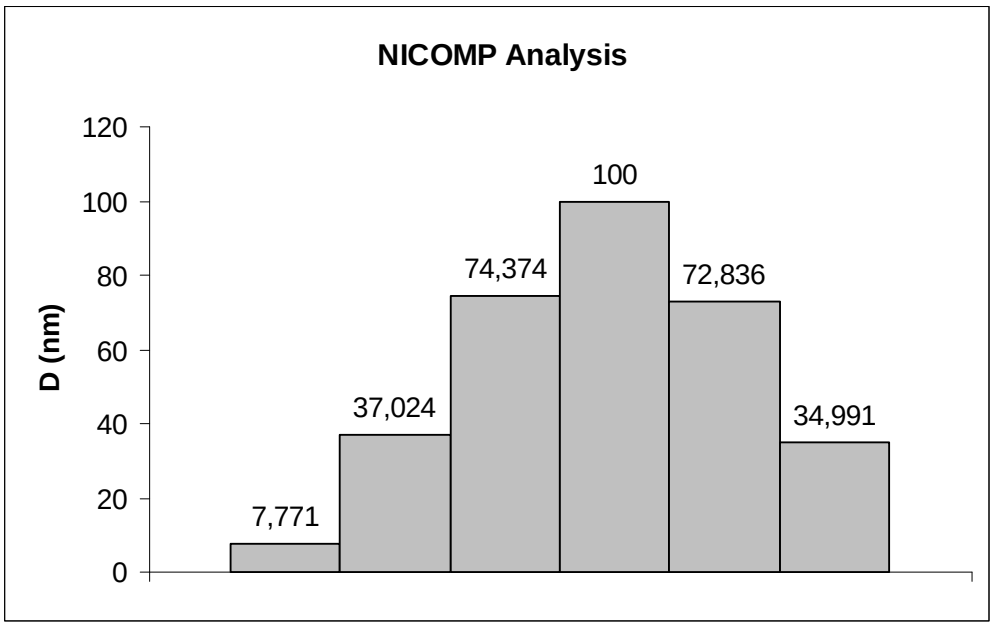

Fig.2 Hybrids particle dimensions distribution from the mixture MPTS/TEOS 50/50 (MPEG 2000)

The obtained results are in good concordance with the one previously published (10), the increase of the hydrophobicity components which participate to the sol-gel particles forming determines the increase of the final dimensions.

The same decreasing effect of the medium dimensions with the increase of the MPTS concentration, have been observed even in the case of the stabilized particles with a nonionic surfactant $NPEO_{25}$ (Fig.3). Metacryloyl hydrophobic component (Fig.1), changed with nonylphenyl, (Fig.3) affects the particles stabilization in the last case, and their dimensions are bigger. In both cases, the obtained dispersions remain stable until 1 year from the storage. They can be used for the obtaining of polymer hybrids through metacryloyl groups copolymerization with similar radical polymerizable groups from different monomers (8).

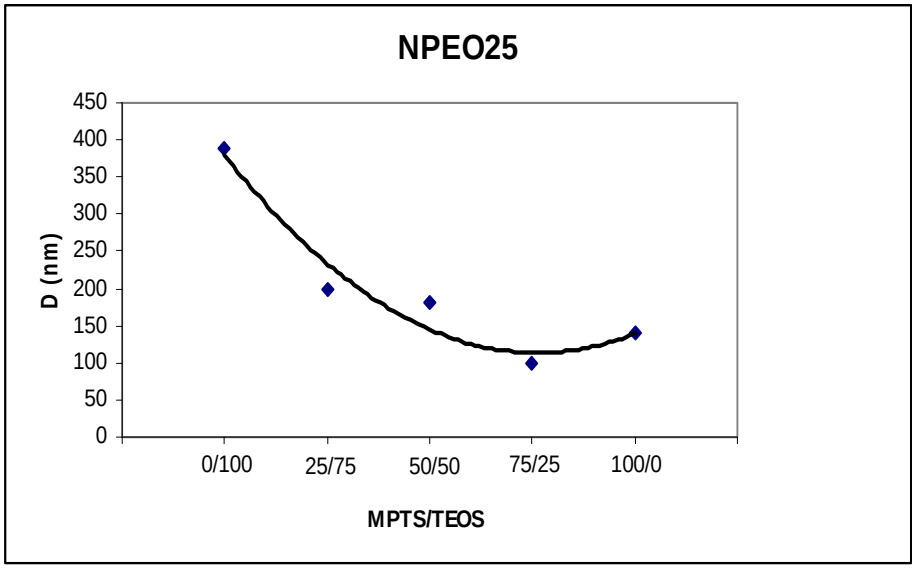

Fig.3 The influence of the ratio MPTS/TEOS from the initial mixture, on the particles medium diameters obtained in the $NPEO_{25}$ presence.

In the same time with the modification of the particle dimensions, the changing of the ratio MPTS/TEOS affects also their Zeta potential (Fig. 4). The MPTS concentration increase, determines the particle's hydrophobic groups increase (11). In the basic medium in which they have been synthesized, the residual SiOH groups remain ionisable from an incompletely condensation process (1). Because the probability that the concentration of these groups will increase with the increasing of the TEOS concentration, it is normal for the Zeta Potential to become more negative in the same time with the partners ratio modification. These observations are in good concordance with the other author's results (12).

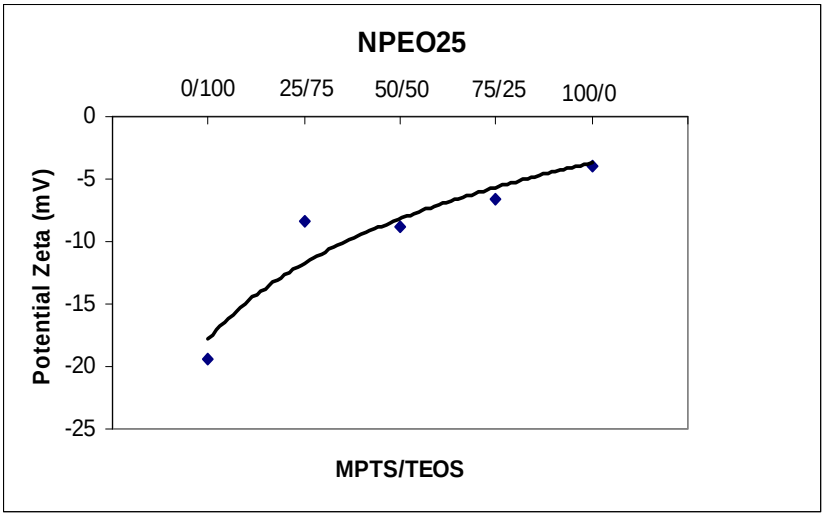

Fig.4 The increase of Zeta potential of hybrids particles with the increase of MPTS concentration from the initial mixture (MPTS/TEOS- (g/g), NPEO25)

4. Conclusions

Modified silica particles with metacryloyl groups, obtained through sol-gel process of MPTS-TEOS have medium diameters which decrease with the trialcoxysilane derivate concentration.

The use of an nonionic surfactant in which the metacryloyl groups are the hydrophobic side as the one from MPTS, have as result smaller particles than the one with $NPEO_{25}$ obtaining. The Zeta Potential increases with the increase of TEOS tetraethoxysilane derivative concentration.

R E F E R E N C E S

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