INORGANIC-ORGANIC HYBRIDS FOR ADVANCED COMPOSITES OBTAINING♦

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Received: 05/05/2008
Accepted after revision: 23/06/2008

♦ Paper presented at the fifth edition of: "Colloque Franco-Roumain de Chimie Appliquée – COFrRoCA 2008", 25 – 29 June 2008, Bacău, Romania.

Abstract: Hybrid inorganic-organic nanocomposites were synthesized in order to subsequently generate silicon nitride by carbothermal nitridation. We intended to obtain in this manner an extraordinary ceramic material, with important characteristics: thermal resistance over 1400 °C, small dilation modulus and reduced friction coefficient.
The radical polymerization of acrylonitrile took place in nanoporous silica, by the initiation with azoizobutirodinitrile (AIBN). It was intended to enhance the homogeneity between constitutive parts by a larger period of imbibition of the silica with the monomer, through a better absorption capacity of the silica for the monomer and by the application of ultrasonication technique. In the work different silica samples were used, in different polymerization conditions, by varying the monomer imbibition period and the ultrasonication time. The nanoporous silica and the obtained nanocomposites were analyzed by various methods: BET, DTA, DSC, TEM, SEM, FTIR and XRD.
The following conclusions were drawn: ultrasonication is a better way to homogenize the constitutive parts of the hybrid materials; the structural homogeneity of nanocomposites is influenced by the purity of samples; a great importance has also the nature of the mineral acid used for the acid attack of the serpentinite.

Keywords: *nanocomposites, hybrids, polymers, special ceramic, template polymerization*

INTRODUCTION

Hybrid inorganic-organic composite is one of the most important categories of synthetic materials. The synthesis and the applications of inorganic-organic nanohybrids were developed mainly in the last decade. The properties of obtained hybrids depend not only on the properties of the individual components, but are also greatly influenced by such factors as phase's size, shape and interfacial properties [1].
Research into the preparation of ceramics from polymeric precursors is generating a great deal of interest because it allows the use of several attractive polymer forming techniques [2]. According to a company leaflet [3], an extraordinary ceramic material is silicon nitride having important characteristics: thermal resistance over 1400 °C, small dilatation modulus and reduced friction coefficient.
Among the known silicon nitride synthesis ways, a main one is the carbothermal nitridation reaction, consisting in silica heating with carbon in nitrogen or ammonia atmosphere [4]. In this reaction an intimate mixture between silica and carbon is essential for the developing in good conditions of nitride synthesis reaction. A method yields an intimate mixture between silica and carbon, by filling of carbon nanotubes with silica [5]. Another method starts from sepiolite hollow fibers in which polymer synthesis takes place, with subsequent carbonization of the polymer [6]. The polymer

must be a carbochain one (the chain must be formed exclusively by carbon). Such carbochain polymer can be obtained by the vinyl monomers polymerization [7].
The present work intends to obtain silicon nitride by carbothermal nitridation, starting from nanoporous silica, in which the acrylonitrile polymerization proceeds, followed by the subsequent transformation of polymeric nanocomposite in silica-carbon nanocomposite. In order to enhance the homogeneity between constitutive parts of the nanocomposite it was tried to increase the imbibition period of the silica with the monomer, to have a better absorption capacity of the silica for the monomer and to use the ultrasonication technique.

MATERIALS AND METHODS

The present work uses as raw material the serpentinite, a soft magnesium silicate rock (Mohr hardness about 3) resulted as sterile mass from the previous mining exploitation of asbestos and found in several dumps in the Natural Park „Porțile de Fier", on the Danube border. As vinyl monomer we use p.a. Merck acrylonitrile, recently distillated, and p.a. Merck azoizobutirodinitrile as initiator of polymerization.
The processing took place in 5 steps. The first step was the grinding of serpentinite. The second step was the nanoporous silica obtaining by the attack of serpentinite with concentrated mineral acid (HCl and HNO_3). The third step consisted in inorganic-organic nanohybrids preparation by template polymerization of acrylonitrile in silica pores. The forth step was the cyclization and graphitization of the carbochain polymer in order to obtain silica-carbon nanocomposites as uniform as possible, and the last step consisted in the conversion into silicon nitride by carbothermal nitridation.
The radical polymerization of acrylonitrile took place in nanoporous silica, by the initiation with azoizobutirodinitrile (AIBN). In order synthesize polymer hybrid nanocomposites the following operations performed: the preparation of the initiator solution in monomer, the imbibitions of monomer with silica, the polymerization at 60 – 65 °C and, finally, the grinding of the hybrid composite. The operations consisting in ultrasonication I: 1 hour, static imbibition with monomer: 22 hours and ultrasonication II: 1 hour, were performed at room temperature. Polymerizations were performed in glass ampoules, sealed, with a Hoffman clamp, after 10 minutes purging with a low flow of nitrogen.

RESULTS AND DISCUSSIONS

Three different silica samples were prepared from grounded serpentinite by the attack with HNO_3 50% in different conditions. The synthesis conditions and chemical composition of the obtained silica are presented in Table 1.
As one can see on Table 1 the synthesis conditions: liquid : solid ratio (L : S), temperature and reaction time influence the purity of the obtained silica. The highest purity was obtained by the acid attack in the most drastic conditions: ratio L : S 6.0, temperature 85 °C and reaction time 120 min. This silica (RN 18) presented the highest monomer absorption too: after the second utlrasonication the monomer is completely absorbed and no monomer film on top of the inorganic material was observed. If the

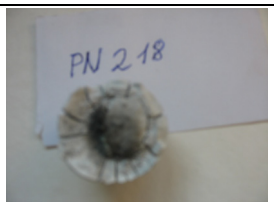
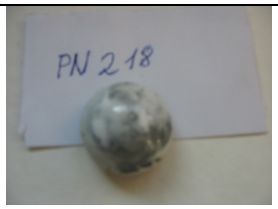
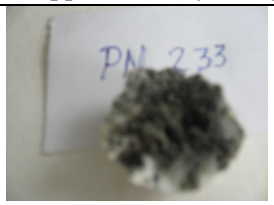
same silica sample is statically imbibited with the monomer during 24 hours, the monomer film is observed. This shows the favorable effect of the ultrasonication on the monomer absorption in silica sample. The ultrasonication effect on the absorption is influenced by the preparation conditions for the silica samples: RN 31 and RN 33 shown a liquid film on the top of the inorganic layer, after the second ultrasonication, even if this film was thinner that in the case of the static imbibition.

Table 1. *Chemical composition of the silica obtained by the attack with HNO_3 50%*

		Code		
		RN18	**RN31**	**RN33**
Synthesis parameters	L : S ratio	6.0	6.0	3.5
	Temperature, °C	85	50	70
	Time, min	120	120	30
Chemical composition, %	SiO_2	70.6	63.7	66.5
	Fe_2O_3	2.3	3.6	3.7
	NiO	0.03	0.05	0.07
	Al_2O_3	1.9	2.1	2.2
	Cr_2O_3	0.9	1.3	1.3
	MgO	2.7	10.1	8.7
	Na_2O	0.2	0.1	0.1
	CaO	0.1	0.1	0.1

The polymerization of acrylonitrile in silica samples, after the ultrasonication allowed obtaining composites. The composites aspect is presented in Table 2.
Comparing the pictures in Table 2 one can observe a great similitude: surface with cracks, the bottom glassy with black spots and interior with black parts. All these facts show that the introducing of ultrasonication stages at the beginning and the end of the imbibition phase didn't lead to uniform composite if the polymerization occurs in static conditions. No influence of silica obtaining conditions on the composites aspects was releaved, all the samples containing black sides, probably with less acrylonitrile content.
The nanoporous silica and the obtained nanocomposites were analyzed by various methods: BET, DTA, DSC, TEM, SEM, FTIR and XRD.
In the following figures, SEM photography of silica sample treated with HCl (Figure 1) and the corresponding nanocomposite (Figure 2) are presented. The images prove the porous structure of the silica and of the polymer composite and the pore dimension between 2 – 20 nm.

Table 2. *The top, bottom and in crack aspect of the polymer nanocomposites obtained from different silica samples*

Silica Sample code	Aspect		
	Upper side	**Bottom**	**Crack**
RN18			
	The top with cracks, the bottom regular with black spots, inside mousy to black, outside white grey.		
RN31			
	The upper side airy and grey, the bottom is glassy with black spots, interior grey.		
RN33			
	The upper side almost airy, the bottom is glassy with black spots, the interior with black isles.		

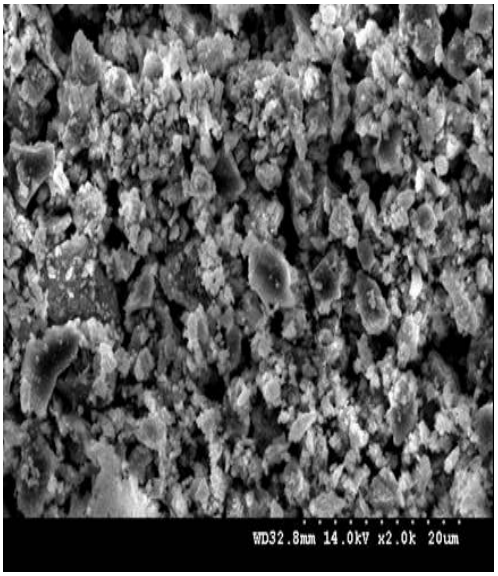


Figure 1. *SEM analysis of silica RN 55 (obtained with HCl)*

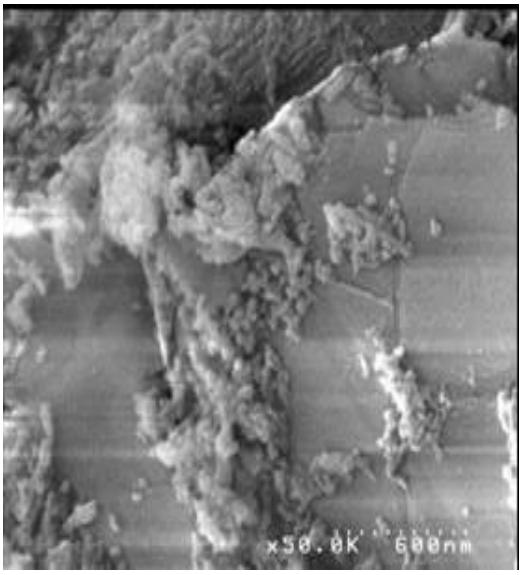


Figure 2. *SEM analysis of nanocomposite obtained from RN55*

CONCLUSIONS

The following conclusions can be drawn:
- Ultrasonication is a better way to enhance the monomer absorption in nanoporous silica;
- The monomer absorption in silica depends of the preparation conditions for silica samples;
- The enhancement of the monomer absorption is not enough to obtain an increased compositional homogeneity of the hybrid nancomposites if the polymerization occurs in static conditions;
- The silica sample and composites have a great porosity.

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