

Characterization of Activated Carbon particles for nanocomposite synthesis.

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ABSTRACT

Activated carbon (AC) micro and nano particles were produced from Granular AC. Particle size distribution was measured before and after THF solvation by light dispersion. Particles were incorporated into a matrix of polystyrene via in situ miniemulsion polymerization. The nanostructured latexes were characterized by TEM and by SEM. Triacetate cellulose (TAC) and AC particles composite membranes were produced and analyzed by AFM tapping® for height and face contrast. Particle size after solvation shows a significant decrease in size. We obtained stable latex with particles of less than 100 nm diameter, TEM micrographs show the encapsulation of the AC nanoparticles into the polystyrene matrices. Integration of AC particles into TAC membranes was successfully done, and AFM images show the nanodispersion of these particles.

Keywords: Activated carbon, miniemulsion polymerization, nanoparticles, AFM.

1 INTRODUCTION

Activated carbon from inexpensive sources has been of great interest for separation systems, especially in the field of water treatment [1]. Efforts had been made to produce AC nanoparticles by different means, in the aim to integrate them to composite materials to enhance their characteristic efficiency [2,3,4]. The success of these applications strongly depends on the availability of colloidal particles with tightly controlled size and surface properties and therefore there is a continuously increase research effort in the synthesis of colloidal carbon micro and nano particles and the methods for characterize them [5]. Numerous reports on the problems to precisely determine the size of these materials have been made [5,6,7,8]. Depending on composition, solvent used or matrix where they are dispersed, these nanosize materials tend to agglomerate in different proportions.

Recently p-aminophenol was synthesized from p-nitrophenol over nanosize nickel catalysts. Size characterization was made by SEM and Mastersizer 2000. Results obtained by light dispersion showed sizes up to six times bigger than the size observed by SEM. One of the reasons for larger particle size measured by Mastersizer 2000 is the presence of extensive twinning and

agglomeration in the samples. In this case, Mastersizer measured the agglomerations instead of crystallites [5].

Miniemulsion polymerization has been successfully used to stabilize different types of nanoparticles, as carbon nanotubes [9], ceramics [10,11], magnetic particles [6, 12] and carbon black [13]. This technique allows the distribution of small concentration of nanoparticles into nanoscale-independent matrices.

Composite materials that incorporate inorganic fillers to polymeric matrices have been prepared for many different applications, specifically the use of activated carbon as filler has drawn attention due to its high adsorbent capacity. ABS copolymer-activated carbon mixed matrix membranes for CO₂/CH₄ separation were produce by casting–evaporation process at 45% relative humidity and showed a simultaneous increase of CO₂ gas permeability (40–600%) and CO₂/CH₄ selectivity (40–100%) by increasing the percentage of carbon loaded in the mixed matrix composite membrane [14].

The adhesion between the polymer phase and the external surface of the particles appeared to be a major problem when glassy polymers are used in the preparation of composite membranes. It seems that the weak polymer–filler interaction makes the filler tend to form voids in the interface between the polymer and the filler [15]. Various techniques have been employed to improve the polymer–filler contact, among them sonicated baths [7,16] and particle surface modification [7] are widely used.

Recently a very inexpensive method to produce AC nanoparticles by solvation was proposed [3]. The objective of this work is to study this production of AC micro and nanoparticles and to study different methods to characterize their average particle size and the possibility to fully disperse them into a polymeric matrix.

2 METHODOLOGY

2.1 Materials

Granular AC (Carbochem LQ 1,000; 870 m²/g surface area, 5.75 Å average pore size) was triturated by steel balls mill (8000 Mixer/Mill, Spex Cetriprep) for 10 min. Powder obtained was sieved to separate particles with less than 53 microns, AC microparticles were agitated in tetrahydrofuran (THF, Merck 99%) 0.1g in 100ml for 96 hours for solvation, and finally dried in an oven for 24 hours[3].

For miniemulsion polymerization, the initiator azobisisobutyronitrile (AIBN; Aldrich) was freshly recrystallized from methanol and kept at 5°C until use, sodium lauryl sulfate (SLS; Aldrich) and hexadecane (HD; Aldrich) were used as received. The water was of tridistilled quality.

Triacetate cellulose (TAC; Aldrich) and AC Particles composite membranes were produced by previously reported method, using methylene chloride (Aldrich) [3]. Vapor induced phase separation was carried out at 70% relative humidity at 35 and 45°C.

2.2 Characterization

Particle size distribution was measured before and after the solvation with THF by light dispersion (Malvern Instruments, Mastersizer 2000), with three different solvents (ethanol, water, and water + sodium hexametaphosphate as surfactant).

AC particles were incorporated, into a matrix of polystyrene via in situ miniemulsion polymerization following the procedure described by Lopez et al. [4]. A mixture formed of 0.05 g of AC particles, 20 g of styrene, 0.18 g of SLS, 0.2 g of AIBN, and 0.83 g of HD was added to a glass flask and sonicated for 15 min to disperse the particles. Some drops of this dispersion were studied by scanning electron microscope (SEM). Afterward 80 g of tridistilled water were introduced into a 250-mL, three-necked, round-bottom glass reactor; the sonicated mixture was fed to the reactor to complete the polymerization system, which was sonicated for 45 min to obtain a stable miniemulsion. It is important to mention that ice was added to the sonication bath during the time of dispersion to avoid the occurrence of free-radical polymerization induced by the high shear strength. Finally, the reactor was immersed into a heating bath (at 60°C). The polymerization was allowed to react for 180 min.

The nanostructured latexes were characterized by TEM with a Philips CM200 operated at a 200-kV accelerating voltage, and by SEM with a JEOL, JSM 5800-LV. Triacetate cellulose (TAC) and AC particles composite membranes were analyzed by AFM tapping® (Nanoscope IV, Digital Instruments) for height and face contrast characteristics. Silica coated phosphorus tips model RTESP (Veeco®), and scan rates of 2–3 Hz were used. Set point and the gains were adjusted to obtain the best image resolution.

3 RESULTS

3.1 Light dispersion

The average particle size measured by light dispersion after THF solvation with the use of a surfactant shows a significant decrease in size (Table 1), but still these results do not fall into the nano scale (below 100 nm). Previous results of TEM micrograph analysis (images not shown) suggest that some of these particles detected by laser

diffraction are in fact particles agglomerates. This is the reason for the larger size detected in the same instrument when different solutions are used (water, and ethanol).

Suspension		Particle Size distribution (80%) μm	mean size μm
Before THF	Surfactant	1.89 - 33.58	8.52
After THF	Surfactant	0.6 - 25.48	1.6
	Ethanol	33.35- 89.76	42.6
	Water	45.8 - 220	98.4

Table 1: AC Particle size distribution, measure by light dispersion.

3.2 Miniemulsion polymerization

AC particles were successfully dispersed in the mixture of styrene and surfactants by 15 minutes sonication. On SEM micrographs we observed different sizes of particles, ranging from micrometers (Fig.1) to less than 400 nm (Fig.2).

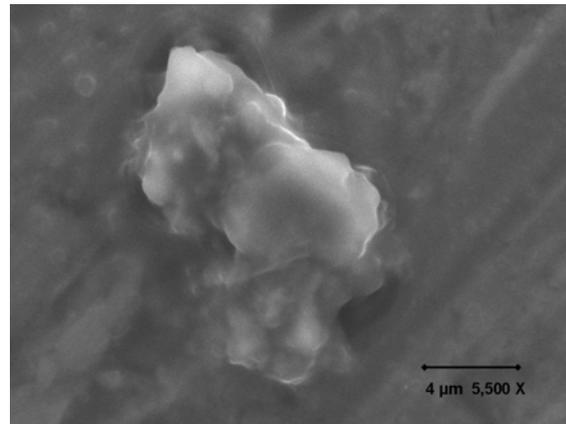


Figure 1: SEM micrograph of AC particles after THF solvation.

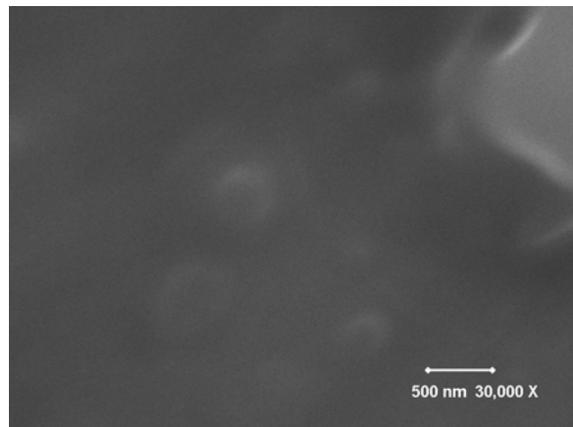


Figure 2: SEM micrograph of AC particles after THF solvation.

Tetrahydrofuran (IUPAC name: Oxacyclopentane) with the formula $(\text{CH}_2)_4\text{O}$ is a heterocyclic organic compound, a strong solvent that dissolves a wide range of non-polar and polar compounds. Activated carbon is a highly porous non-polar solid that can be easily penetrated by THF and dissociated into smaller particles by means of solvation. Previous studies reported the effect of strong solvents like dimethylformamide (DMF) on the casting of composite membranes with activated carbon particles; SEM images of the AC particles indicated an increase in particle channelling and size decrement due to the close contact of solvent and particles during polymer dissolution [15].

During our experiment the contact time between THF and AC particles was enough to let the solvent penetrate into the porous structure and led to partial fragmentation of the particles. Nevertheless this fragmentation was by non means uniform since SEM micrographs clearly shows a very wide particle size dispersion.

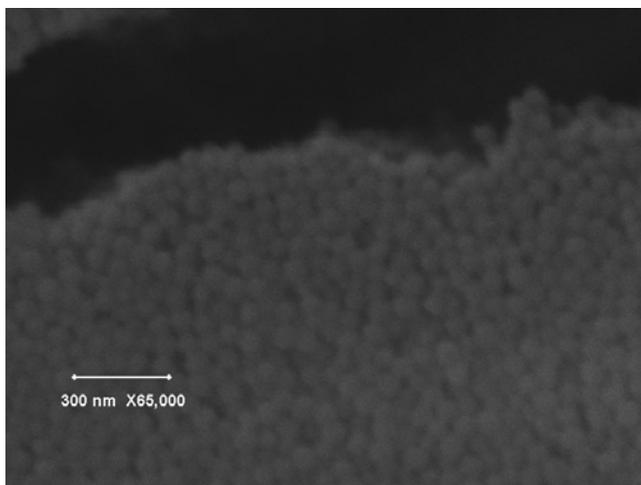


Figure 3: SEM micrograph of AC/polystyrene nanocomposite.

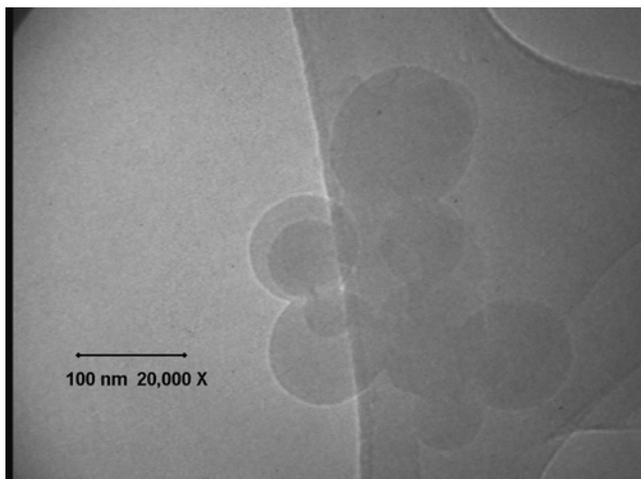


Figure 4: TEM micrograph of AC/polystyrene nanocomposite.

By miniemulsion polymerization stable latex with particles of less than 100 nm diameter was obtained (Fig.3), and TEM micrograph shows the encapsulation of the AC nanoparticles into the polystyrene particles (Fig.4). It is important to realize that some AC particles were not integrated into the miniemulsion, and were precipitated during the polymerization, which indicate that there were still a good amount of AC particles that were bigger than 100 nm.

3.3 Membrane characterization by AFM

Integration of AC particles into TAC membranes was macroscopically homogenous. With the aid of an optical microscope integrated to the AFM the scanning of the surface was made only where there were not micrometric AC particles. Fig. 5(a) shows an AFM topographic image obtained from the height signal, scan area of $2 \mu\text{m}^2$. Valleys and peaks are clearly distinguished by color pallets, darkest areas represent porous formed in the membrane during the casting process; light color areas indicate either nodules formed by the polymer or presence of AC particles.

Face contrast images obtained from AFM are a powerful extension of the tapping mode® (Digital Instruments, Santa Barbara, CA), since they provide information at nanometric scale about the surface structure and some characteristics that are not regularly revealed by other microscopic techniques. By register the delay on the cantilever oscillation on tapping mode, the obtained images detect variations on composition, adhesion, friction, viscoelasticity among others.

Face contrast image of the exact same area (Fig. 5b) reveals the presence of two different materials, corresponding to the polymer TAC (dark homogenous areas) and AC particles (light, granular shape areas).

AC particles can be distinguished and size range is from 4 nm to 220 nm. Grain analysis from each image was made with software Nanoscope 5.30r3sr3®, Fig. 6 shows the particle size distribution obtained. Data from this analysis indicate a particle mean size of 19.53 nm and a standard deviation of 1.87 nm. Nanodispersion can be seen on every image obtained of all the membranes prepared.

4 CONCLUSIONS

Activated Carbon solvation in THF produced micro and nano-particles due to fragmentation, resulting in wide particle size dispersion. Results obtained by light dispersion shows a decrement of particle size, but the use of different solvents in the experiment can lead to confusion since particles tend to agglomerate.

AC particles disperse well in styrene and surfactants, SEM micrographs show particles of different sizes in both micro and nano scale. Stable latex with particles of less than 100 nm diameter was obtained, TEM micrographs show the encapsulation of the AC nanoparticles into the polystyrene particles. Integration of AC particles into TAC

membranes was successfully done, and AFM images show the nanodispersion of these particles.

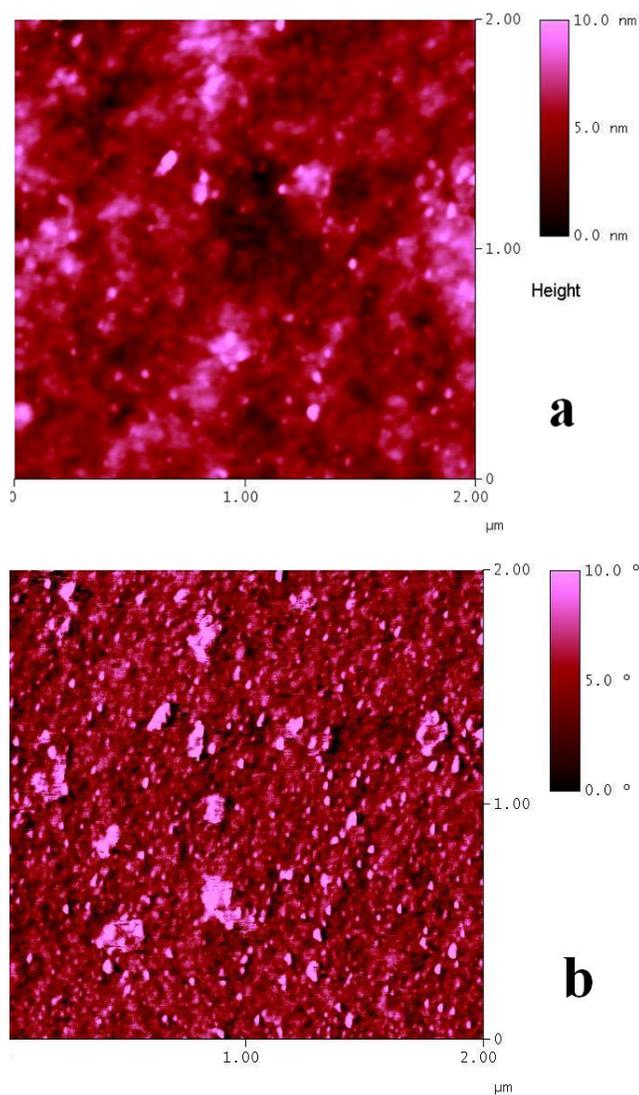


Figure 5: AFM images of CTA/AC composite membranes obtained at 70%RH. (a) topographic image, (b) phase contrast image. Scanning area of $2 \mu^2$.

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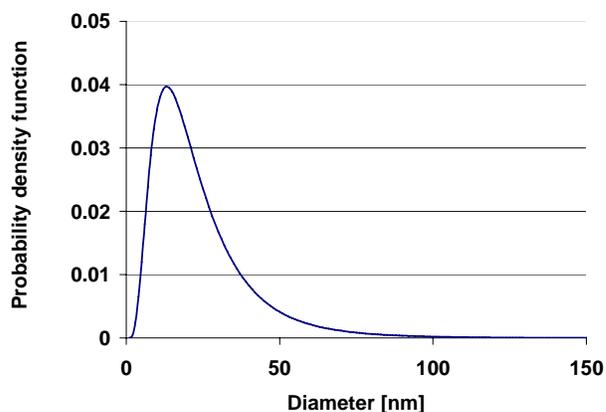


Figure 6: Particle size distribution from AFM images analysis.

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