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Investigation of the Effect of Nano-Alumina Particles on Adsorption Property of Acrylic Fiber

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***Abstract*—**The flue gas from fossil fuels combustion contains harmful pollutants dangerous for human health and environment. One of the air pollution control methods to restrict the emission of these pollutants is based on using the nanoparticle in adsorption process. In the present research, gamma nano-alumina particle is added to polyacrylonitrile (PAN) polymer through simple loading method, and the adsorption capacity of the wet spun fiber is investigated. The results of exposure the fiber to the acid gases including SO_2, CO, NO_2, NO, and CO_2 show the noticeable increase of gas adsorption capacity on fiber contains nanoparticle. The research has been conducted in Acrylic II Plant of Polyacryl Iran Corporation.

Keywords—Acrylic fiber, adsorbent, wet spun, polyacryl company, gamma nano-alumina.

I. INTRODUCTION

CURRENTLY, nanoparticle research is a very promising scientific research due to the wide range of potential and promising applications especially in biomedical, optical, and electronic fields [1].

Nanoparticles are building the bridge of the scientific knowledge connecting bulk materials to atomic or molecular structures. This new field of science converts the previous science theories and principles to prove that the properties of materials change as their size approaches to the nanoscale. As a result, the percentage of atoms at the surface of a material becomes significantly smaller. This new concept changes the use of such material in micro scale size to be used in absolutely new and advanced applications by using a nanoscale size of the same material.

This section describes briefly the complexity of alumina crystalline phases and reviews the properties of the three phases which are encountered in this work [2].

A. Alumina Polymorphs (A Conundrum)

Alumina exists in a number of crystalline phases (polymorphs). Three of the most important ones are γ, θ, and α.

The α structure is thermodynamically stable at all temperatures up to its melting point at 2051 °C, but the metastable phases (e.g., γ and θ) still appear frequently in alumina growth studies for reasons that are discussed in the following sections.

The common alumina polymorphs can all be formed within typical synthesis temperatures, but the polymorphism also opens many opportunities for applications in various areas of technical science, since the properties of one alumina phase in some respects differ from the properties of another, as described in the following sections. All alumina phases are involved in transformation sequences, which all have in common that they end in the α phase at high temperature.

The transformations to the α phase are irreversible and typically take place at above 1000 °C.

B. Properties of α-Alumina

The α form of aluminum oxide is also known as corundum (the name comes from the naturally occurring mineral corundum, which consists of pure α-Al_2O_3). It is transparent and uncolored and is known in its single crystal form as sapphire. It is used not only in materials science, but it occurs also as gemstones. The gem known as ruby is α-alumina doped with small amounts of chromium, while the gemstone sapphire is actually α-alumina doped with iron and titanium.

Like all alumina phases, the α phase is highly ionic with calculated valences of +2.63e and –1.75e for aluminum and oxygen, respectively. Thus, the chemical bonds between ions are almost purely ionic (or electrostatic), a fact that is closely related to the structural behavior of alumina. The α alumina is the only stable alumina phase at all temperatures. It has a trigonal (rhombohedral) structure (R-3c) and is usually described as ABAB stacking of oxygen planes along the c direction. Rhombohedral phase of alumina can be described as a hexagonal close packed (HCP) oxygen sublattice, in which the aluminum atoms, or ions, occupy two thirds of the octahedral interstices, i.e. they have six oxygen nearest neighbors, so that there is only one coordination (octahedral) for aluminum and one for oxygen (with four surrounding aluminum ions) exists.

C. Properties of θ-Alumina

The θ phase of alumina is metastable and transforms into α phase at about 1050 °C. It is less dense than the α phase with a density of about 3600 kg/m^3 compared to 4000 kg/m^3 for α-alumina. The structures of all alumina phases are built up around (slightly distorted) close-packed oxygen lattices and while α phase has an HCP framework, the θ structure is based on an FCC oxygen lattice. Within this oxygen framework, half of the aluminum ions occupy octahedral interstitial sites, and half occupy tetrahedral (with four oxygen neighbors) sites. This is also in contrast to the α phase.

The oxygen ions have three different possible surroundings, each of which is occupied by one third of the oxygen ions. Two of these oxygen sites have three aluminum atoms in

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nearest neighbors, and the third one has four. The structure is monoclinic, belonging to space group C2 /m, and the unit cell contains four formula units (20 atoms) with lattice parameters. θ alumina is a structural isomorph of β-Ga_2O_3 and, interestingly, gallium oxide can also form the corundum structure. There are not as many investigations made on the θ phase as on α alumina. It is clear, though, that it is highly ionic and insulated with a band gap of 7.4 eV.

D. Properties of γ-Alumina

Due to low surface energy and hence high surface area, γ alumina is extensively used as catalyst supports. The low surface energy also means that the γ phase is surface energy stabilized when the surface area is high relative to the bulk volume, e.g. for small grain sizes. For high temperature applications, a problem with the use of the γ phase is that it transforms into θ at 700-800 °C. This has led to the experimental research on doping of alumina to increase its thermal stability. The γ alumina structure has two main similarities with the θ phase, the FCC oxygen lattice and the mixture of octahedral and tetrahedral coordinated aluminum ions. However, the exact structure is not well defined. It is commonly believed that the structure can be described as a defect cubic spinel with space group Fd-3m and is based on an FCC, ABCABC stacking of oxygen. The aluminum ions are more or less randomly distributed between octahedral and tetrahedral sites. Each unit cell contains 32 oxygen and 64/3 aluminum ions to fulfill stoichiometry. The aluminum ions occupy both octahedral and tetrahedral positions, but the relative partial occupancy in each position is still a matter of dispute.

II. MATERIALS AND METHODS:

A. Nanoparticle

The physical properties of nanoparticle as follows:

- Assay: More than 99%
- Average Particle size: 3-8 nm
- Specific Surface Area: 130-270 m^2/gr
- Bulk Density: 125 kg/m^3
- Crystal Structure: Cubic
- Rhombohedral Particle Morphology: Nearly Spherical
- Appearance Form: Powder
- Color: White
- Chemical Composition: Ca, Na, Si
- Prevailing phase: Al_2O_3 (γ)

B. Polymer

The spinning process is largely influenced by the characteristics of the polymer solution, also known as the spinning dope. Spinning dopes are produced using various organic and other solvents. Solvents used to make spinning dopes often have polar molecules with large dipole moments and low molecular weights. Some of the most common solvents used include dimethylformamid (DMF), dimethylacetamide (DMAc), and dimethylsulfoxide (DMSO). Dimethylformamid and dimethylacetamide and they tend to be the most commonly used solvents in commercial production.

PAN is prepared by solution polymerization of acrylonitrile (AN) and vinyl acetate (VA) in DMF solvent.

Polymer composition was: 21% PAN, 2%H_2O, and 77% DMF, with density 920 kg/m^3 and absolute viscosity of 4485 CP.

C. Spinning

One of the most important parameters of adsorbent fiber is the high porosity. Wet spun acrylic fibers are very porous because the porosity and cross-sectional area of the fibers depend on DMF and water concentration, bathes temperature and draw ratio (see Fig. 1).

The first affecting parameters on product quality of acrylic fiber process by wet spinning were recognized with literature review [1], [2], [5], [6].

Important parameters that have great effect on porosity in spinning section are:

1. Total stretching ratio
2. Coagulation bath composition and temperature
3. Stretching bath temperature
4. Crimper condition
5. Drying temperature and residence time in dryer

Important parameters in chemical area include solid percentage (%PAN) in polymer, water percentage, and average molecular weight. Viscosity of polymer and etc. are ignored.

Microvoids produced in wet spinning are considered to be an important factor for its better adsorption.

Surface area is measured to be in range of 100-250 m^2/gr for wet spun, whereas that for dry spun is less than 1 m^2/gr.

The main effect of the coagulation parameters on the fiber structure is the filaments porosity. A macro porous structure, due to the presence of big voids, reveals a non-homogeneous structure between the skin and the core, which persists during all the spinning process. On the contrary, a micro porous structure, evidence by a very fine reticular structure, can be compacted in drying phase, giving rise to a homogeneous final structure.

In the first case, during the coagulation step, the diffusion rate of the solvent and non-solvent through the fiber surface is similar. In the second case, the solvent diffusion speed prevails. The faster the coagulation, the higher the fiber porosity is, and thus its dullness.

The coagulation bath composition has a great influence on the production of voids.

For DMF concentrations below 50%, coagulation occurs quickly, giving rise to considerable water diffusion inside the fiber during its formation. This phenomenon generates a great number of voids due to the breakage if the skin is produced in coagulation.

The best conditions for the industrial process have been found at a concentration of about 55% DMF, where the spinneret stretch is high. In fact, in these conditions, the coagulation speed allows a reliable spinning, and the number of voids is low so that the mechanical and brightness characteristics of the final fiber are not affected.

If the DMF concentration is in the range 60-80%, the fiber is not fit for spinning: in this range the mixture H_2O/DMF reaches a maximum viscosity because the association of 2 moles if H_2O with 1 mole of DMF.

If the DMF concentration is over 80%, coagulation takes place very slowly. Practically, there is no skin production and the water, which tends to flow into the fiber very slowly, produces a great number of micro voids. For DMF concentrations>90%, no coagulation occurs (Fig. 1).

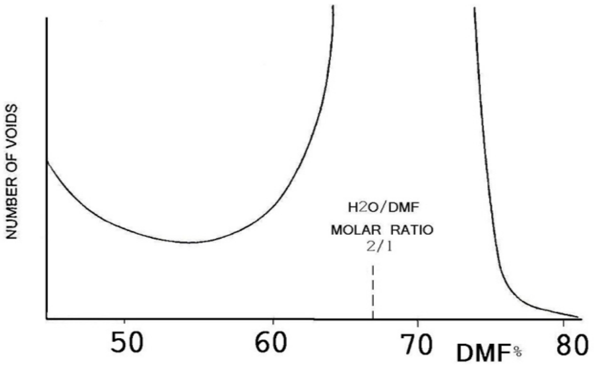

Fig. 1 Number of voids vs. %DMF in the coagulation bath

Temperature of the coagulation bath: Having the same bath composition (DMF 55%), the fiber compactness increases, and the number of voids is reduced whenever the bath temperature decreases. This phenomenon can be explained considering the effect of temperature towards the coagulation rate.

Stretching ratio and temperature of stretching bath: The possibility of stretching the fiber depends on its temperature during the stretching step (see Fig. 2) [4], [6].

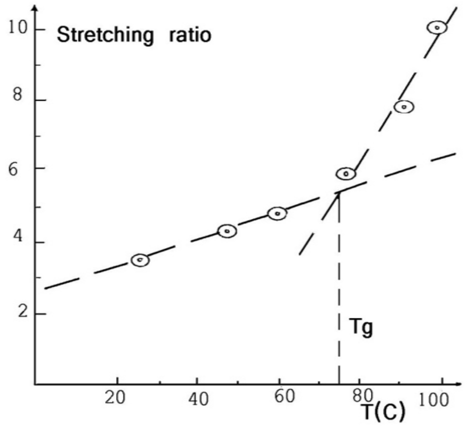

Fig. 2 Maximum stretching ratio (final speed=collection speed) vs. temperature of the stretching bath. Tg=wet glass transition temperature of the fibers

The diagram clearly shows a slope increase, and therefore an increase in the stretch ability, over the wet second order transition temperature of fiber.

It is important to remember, however, that it is advisable to use the proper temperature for each stretch ratio: lower temperatures than necessary cause broken filaments, but too high temperatures cause an irregular stretch, with negative effects on fiber properties and its variation coefficients.

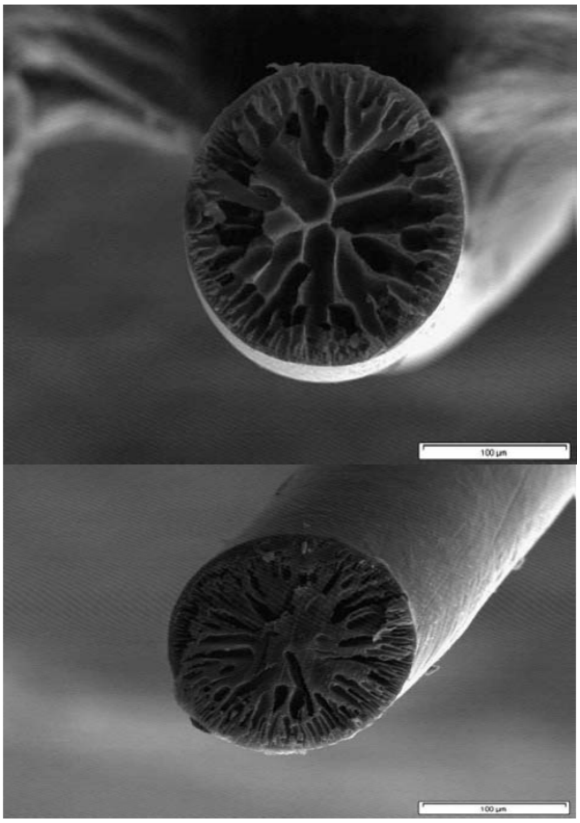

Fig. 3 Cross-section and porosity morphology of as-spun PAN fibers

D. The Methods Used to Mix Nanoparticle with Polymer

Generally porous solids with high surface area are the best choice to use as adsorbent. Acrylic fiber produced by wet spinning has high porosity and can be suitable adsorbent. Different methods are used to mix nanoparticle and polymer. The most common ones are [3], [4]:

1) Simple Loading (Mixing)

This is a simple and standard method. The porous adsorbent is added to the polymer solution and stirring is done for certain time then the mixture left for one hour, and the resulting master batch is used.

2) Solvent Vaporization

In this method, a certain adsorbent is added to the polymer solution in control condition, then the solvent is evaporated. In this method, loading is done in special condition.

3) Vacuum Loading

Adsorbent is added to the polymer solution, and the mixture is placed under vacuum for one hour. Then, filtering is done.

In this research, simple loading has been used. Dope, DMF and nanogamma alumina particle were mixed in a stirred tank. The master batch with 10% nanogamma alumina was obtained, and the filtration and storage has been done. This master batch has been injected to main spinning line to produce acrylic fibers.

The mechanism of PAN fiber formation by the wet-spinning technique is quite complex and involves a combination of rheological and diffusion phenomena. In summary, wet spinning involves passing the polymer from spinnerets and coagulation bath, washing, stretching drying crimping and handling to the final product and packaged on tow or staple. Fig. 4 shows the schematic of the process by wet-spinning: [5], [6].

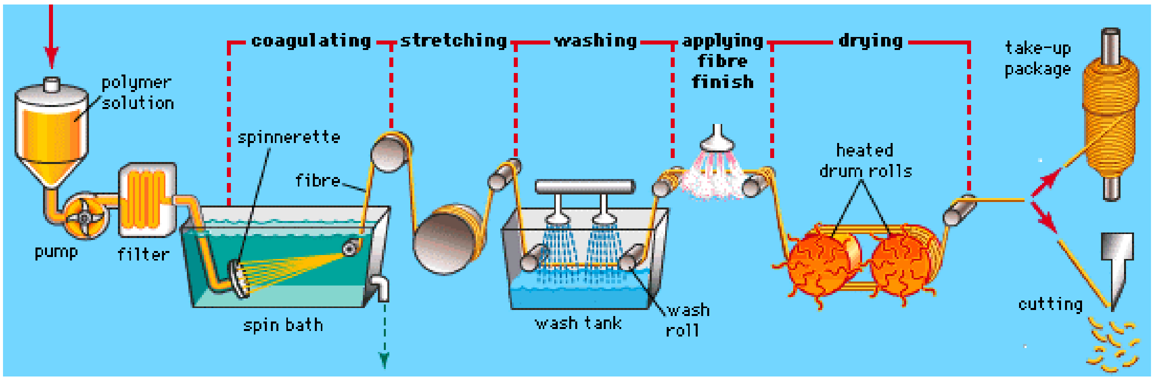

Fig. 4 Acrylic fiber production by wet-spinning

After passing the polymer from spinnerets, coagulation bath, pre-stretching bath, washing bath, stretching bath and dryer, fibers containing nano alumina particles are produced. Titan existence in fiber leads to continuous migration in nanoparticles to fiber surface. A texture has been prepared from these fibers and in an isolated chamber with exposure to flue gas.

Gas concentration measuring was done using Testo 350 XL analyzer from Bühler Company. The device consists of two parts Analyzer and Control-Unit, using input and output gas concentration adsorption the amount of adsorbed gas can be calculated.

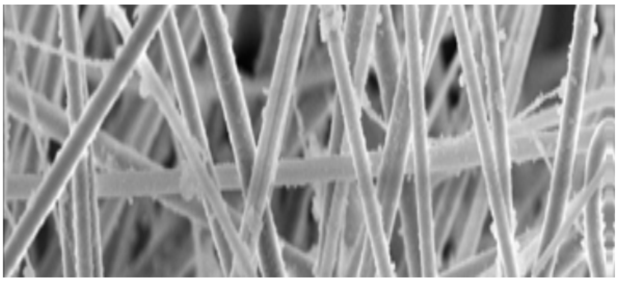

Fig. 5 SEM images of aluminum nanofiber formed on the surface of micron glass fiber (Johnson-Manville, 110X)

III. Result and Discussion

Exposing the adsorbent fibers containing gamma alumina particle to the flue gas and calculating the amount of gas concentration decrease, the following results obtained:

- Specific surface area: (150 m^2/gr)
- CO gas: concentration reduction 7.5 %
- CO_2 gas: concentration reduction 7.3 %
- NO_2 gas: concentration reduction 6 %
- SO_2 gas: concentration reduction 3 %

Because of high porosity in wet spun acrylic fiber that leads to continuous migration of nanoparticle from micro voids to fiber surface, suitable and acceptable adsorption occurs. In Fig. 5, the effect of adding nanoparticle on fiber structure in SEM images is shown [4].

IV. Conclusion

In this paper, the effect of nanoparticle existence on adsorption properties of acrylic fiber was investigated.

Migration of nanoparticle through micro voids to fiber surface leads to increased adsorption capacity in wet spun acrylic fibers because of high porosity the migration is intensified. The results show the positive effect of nanoparticle existence in fiber on amount adsorbed gas.

In future research: other loading methods, the effect of operating parameters on adsorption (temperature, pressure,…) and adsorption modeling using mass transfer balances will be will be investigated.

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