Synthesis of PANi-SiO2 Nanocomposite with In-Situ Polymerization Method: Nanoparticle Silica (NPS) Amorphous and Crystalline Phase

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Abstract: Silica which is synthesized from natural materials such as Bancar Tuban’s sand composited with Polyaniline (PANI), where the silica used are silica has an amorphous phase and cristobalite phase. In this research, the composite method used is in-situ polymerization, which is silica entered during the fabrication of PANi, then automatically silica will be substitute into the chain bonding of PANi. The aim of this research is to find out the results of a composite process using in-situ methods as well as differences in the morphology of PANi/a-SiO2 and PANi/c-SiO2. For the characterization of samples tested in the form of FTIR to determine the functional groups of the composite and SEM to determine the morphology of the sample. From the test results of FTIR are known composite possibility has occurred because there are several functional groups belonging to silica also functional groups belonging polyaniline, functional group that’s happened in wave numbers were almost identical between PANi/a-SiO2 and PANi/c-SiO2, but there are little differences were seen in the form of a graph generated from the peak and intensity that occurred charts for PANi/c-SiO2 has peak more pointed or sharp compared to PANi/a-SiO2 because that bond of crystal is strong, stiff and has a larger particle size than the amorphous composite. Then from the data of SEM seen clearly their morphological differences between PANi/a-SiO2 and PANi/c-SiO2 where polyaniline is composited with amorphous silica will have a fault that is not uniform or irregular different from PANi/c -SiO2 has a regular fault and this is corresponding with the nature of the typical structure of amorphous and crystalline.

1. Introduction
Nano materials have attracted much scientific interest due to the potentially new performance of the particles in nanometer (nm) scale or (<10 nm). Silica is synonymous with silicon dioxide (SiO2). Silicon and oxygen are the two most abundant elements in the earth’s crust. Silica is commonly found in nature as silica sand, rock, mudstone, mud vulcano (lusi)[1,2]. Silica exists in many different forms that can be crystalline as well as non-crystalline (amorphous). The SiO2 nanoparticles are pore
material, with a pore size that can be designed, as applicable: micropore, misoporpi and nanopore materials [3,4]. The SiO$_2$ nanoparticles have an amorphous and crystalline phase: quartz, tridymite, cristobalite, coesite, and satishovite [5]. Amorphous silicon is a kind of allotropes of silicon, silicon dioxide or silica with the chemical formula SiO$_2$. Crystalline silicon is usually a tetrahedron, and each silicon atom is at the top of the tetrahedron and bound covalently with four other silicon atoms. This structure can be very large stretched, thus forming a stable lattice structure. And no qualitative silicite is absent in this extended lattice structure, the lattice network between atoms is irregular. Amorphous silica is generally produced: as wet process silica, as dry process, pyrogenic, airborn fumed silica as well as, and as arc furnace silica. [6]. Silica nanoparticles are low-toxicity and biocompatible, also porous materials, so many applications, including: as drug delivery system (DDS) [7,8], as a filler on PANi composite for smart coating [9], corrosion protection [10,11], Self-healing coatings in anticorrosion [12], etc.

PAni has a conductive and non-conductive formation. Conductive polymers have been the topic of a number of major studies over the past decade, due to their unique properties: mechanical strength, electrical conductivity, and corrosion protection. PAni organic materials can be synthesized oxidatively and electrochemically; oxidation states of polyaniline include: leucoemarldine, emeraldine-base, emarldine-salt and pernigranline [10,13,14]. Application of conductive PANI include: solar energy conversion materials, on rechargeable batteries with SiO$_2$@PANi/Ag formation form [15], electrochemical sensor and biosensor [16,17], supercapacitor [18] and active corrosion protectors, smart-coating [9,19], nanowire form for chemiresistive sensing [13], support for battery electrolyte material [20], can also be used in photovoltaic applications [21] and because of its high electrical and thermal stability, this material is also the prospect for organic semiconductor LEDs [22]. PANi can be synthesized by chemical and electrochemical oxidative methods, and PANi/SiO$_2$ Nanoparticles can be synthesized by In-Situ polymerization methods and mixing ex-situ solution [23–25]. Many researchers interested in studying polymer / Nano particle materials, including the most interesting are PANi/SiO$_2$ Nanoparticles [19], the SiO$_2$ Nanoparticles themselves are porous materials in which the size and shape of the porus can be modified according to the purpose of the application. Among the most popular applications currently associated with PANi-conductive/SiO$_2$- nanoparticle materials are as intelligent, anti-corrosion coating material [10]. Composite PANi/SiO$_2$ prepared by In-Situ method, obtained a good surface coating material, able to protect the steel surface against corrosive solution (such as: Strong acids, and high concentration NaCl) [10,19]. The In situ method of synthesizing nanoparticles in the polymer matrix is a simple and effective route for preparing nanocomposites materials. This method allows one step in the fabrication process of nanocomposites by in situ generating nanoparticles of the precursor accordingly. In this case, the nanoparticles can grow inside the polymer matrix. The advantage of this route is to prevent the occurrence of particle agglomeration while maintaining a good spatial distribution in the polymer matrix. The disadvantage of this method is that unreacted in-situ reaction changes can affect the nature of the end product. [25] This study focuses only on the study of PANi/SiO$_2$ composites synthesized by in-situ polymerization methods, in which SiO$_2$ nanoparticles are prepared from silica sand by hydrothermal-co-precipitation methods. SiO$_2$ nanoparticles are prepared for two different phases: amorphous silica (a-SiO$_2$) and crystalline silica (c-SiO$_2$). Finally characterization of the composite material, which includes: functional group analysis with FTIR, crystal structure analysis and phase by X-ray diffraction, marine analysis with SEM.

2. Eksperimental Method
The first step of the research is to prepare the silica sand material as the base material to be processed into amorphous and crystalline phase SiO$_2$ Nanoparticles (NPS); and other chemicals such as aniline, APS, HCl and Acetone for polyaniline synthesis. The coprecipitation-hydrothermal method was chosen as the NPS preparation method in this study. After SiO$_2$ the amorphous phase, furthermore calcination will be obtained by SiO$_2$ crystalline phase. The second step is the formation of PANi/SiO$_2$
composites, where NPS and Aniline are mixed with in-situ process, polymerization process to form PANi; and the final result is obtained by composite material of PANi/SiO2. After composite synthesis is composite characterization with FTIR and SEM. In this study, the manipulation variables used are the amorphous and crystalline silica phases and by controlling the addition of NPS compositions to the PANi/SiO2 composites.

Table 1. The composition of Nanoparticles SiO2 (as fillers)

| Samples | SiO2 (powders) Wt% | Mass (gram) | PANi (Wt%) |
|---------|------------------|-------------|-------------|
| 1       | 5                | 0.10        | 95          |
| 2       | 10               | 0.20        | 90          |
| 3       | 15               | 0.35        | 85          |
| 4       | 20               | 0.50        | 80          |

3. Result and Discussion

3.1 Characterization with FTIR

There are 8 sample result of FTIR test, i.e. composite PANi/a-SiO2 with addition of SiO2 by 5%, 10%, 15% and 20% then PANi/c-SiO2 type with the same filler anyway. Following one of the FTIR results for each of the PANi/a-SiO2 and PANi/c-SiO2. For a moment, both of picture looks the same, even for the wavelength which is just a little bit at odds. But there is a difference in the length of the peak and peak shape in the picture, i.e. length for peak amorphous with filler tend to be shorter and not as high as peak of composite with crystal filler. This indicate that’s structure of crystal filler have bigger vibration than composite with amorp filler. Then from the above data to come by tables for different types of functional groups as follows:

It can be seen in Figure 1 that the infra-red wave absorption peaks for both types of samples exhibit almost identical patterns. Composite samples of PANi/c-SiO2 (crystal) have peaks that tend to be more pointed than the composite peak of PANi/a-SiO2, indicating that the SiO2 bond of the crystal is stronger than the amorphous particles, resulting in widening peaks. The most distinct infrared wave absorption pattern occurred in a sample with a 95 : 5 compositions in wt%, indicating significantly different peak width and height, for a sample of PANi/c-SiO2 more dominantly vibrasini its functional group than for a sample of PANi/a-SiO2. It can also be shown that the pattern of absorption of functional groups in PANi is unchanged for both types of composites, indicating that the addition of the silica particle type as a filler does not affect the PANi structure as a matrix and the characteristic properties of each base material still exist, but in general the strong vibration the functional group indicates the type of polymer bond in the sample of PANi/a-SiO2 and PANi/c-SiO2; the bond profile in the composite will be confirmed further with SEM data.

Infrared wave absorption pattern in the functional groups of PANi and SiO2 can be confirmed and there is a match with the results of previous research, where the absorption pattern occurring in the C-Cl function group in the range of wave numbers 590-700 cm⁻¹ [27] the results of this study samples of PANi/a-SiO2 vibration of C-Cl functional groups occurred in wave numbers 505.37 cm⁻¹, 609.53 cm⁻¹ and 690.54 cm⁻¹ [Table 2]. As for the sample of PANi /c-SiO2 the vibration of the C-Cl bonding function bands occurs at 507.95 cm⁻¹ and 696.33 cm⁻¹ wave numbers [Table 2]. And the vibration of CH bending occurred in the range of wave number 675-900 cm⁻¹ [10, 26], the result of PANi /a-SiO2 sample test showed that vibration of CH bending occurred at wave number 690.54 cm⁻¹ and 881.5 cm⁻¹ ; meanwhile for samples of PANi/c-SiO2 the C-H bending vibrations occur at wave numbers 815.92 cm-1 and 879.57 cm-1. In the wavelength range 800-870 cm⁻¹ is a group on silica [27] which appears on the composite PANi/SiO2 (95% : 5%) both amorphous and crystalline, OH group of SiO2 at wave number 810.13 cm⁻¹ ; whereas for samples PANi /a-SiO2 and PANi /c-SiO2 successively occurred at wave numbers 815.92 cm⁻¹ and 879.57 cm⁻¹ (see Table2).
Figure 1. FTIR Pattern of samples PANi composite with reinforced: (a) amorphous silica (a-SiO₂), (b) crystalline silica (c-SiO₂) Nanoparticles

The CN stretch of benzoid ring bonding function is the absorption of the yeng wave which is the characteristic of PANi-conductive material, with formation to form emeraldine salt [10, 13, 19, 28], and this bond is in the range of 1020-1250 cm⁻¹ [29, 28], in the samples prepared in this study, the CN functional groups occurred at wave numbers 1136.11 cm⁻¹ and 1242.2 cm⁻¹ for samples of PANi / a-SiO₂, and at wave numbers of 1147.68 cm⁻¹ and 1242.2 cm⁻¹ for the sample of PANi/c-SiO₂ [Table 2]. The argument is in conformity with the preceding finding, occurring in the range of 1250-1335 cm⁻¹ wave numbers of C-N stretch of Q-B-Q [30, 29, 31, 32]. The functional group in the sample occurs at the same wave number of 1301.99 cm⁻¹. For the C = C quinoid ring (NBN) in the 1500-1600 cm⁻¹
wave range [30,29] it is also consistent for the sample, which occurs in the range of 1504.53 cm\(^{-1}\), 1537.32 cm\(^{-1}\) and 1593.52 cm\(^{-1}\) for samples of PANi/a-SiO\(_2\); and occurs at wave numbers 1591.33 cm\(^{-1}\). And the vibration of the -OH functional group which is the prior art silica functional group occurred in the range of 3000-4000 cm\(^{-1}\) wave numbers [27] for the composite samples of PANi / a-SiO\(_2\) ie at wave numbers 3203.87 cm\(^{-1}\) and 3392.9 cm\(^{-1}\) and for sample of PANi/c-SiO\(_2\) at 3153.72 cm\(^{-1}\).

### Table 2. FTIR result for amorphous silica (a-SiO\(_2\)) and crystalline silica (c-SiO\(_2\))

| No | Wave Numbers (cm\(^{-1}\)) | Reference | Functional | Reference |
|----|----------------------------|-----------|------------|-----------|
| a-SiO\(_2\) | c-SiO\(_2\) | | | |
| 1 | 597.95 | 597.95 | 590 - 700 | C-Cl stretching | [33, 28] |
| 2 | 619.17 | 648.1 | | | |
| 3 | 702.11 | 705.97 | 675 - 900 | C-H bending | [33, 29] |
| 4 | 879.57 | 879.57 | 800 - 870 | Vibration of O-H from Si-O | [2, 27] |
| 5 | 1147.68 | 1147.68 | 1020 - 1250 | C-N stretch of benzoid ring | [33, 31, 30] |
| 6 | 1242.2 | 1242.2 | | | |
| 7 | 1300.07 | 1301.99 | 1250 - 1335 | C-N stretch of Q-B-Q | [31,30,32,29] |
| 8 | 1573.97 | 1572.04 | 1500 - 1600 | C = C quinoid ring stretch (N-B-N) | [30, 29] |
| 9 | 3169.15 | 3153.72 | 3000 - 4000 | Vibrations of O-H | [27, 34] |
| 10 | 3394.83 | | | | |

#### 3.2 Result test of SEM

Shown in Figure 2, morphologi samples: (a) PANi and enlargement (a1); (b) c-SiO\(_2\); (c) a-SiO\(_2\); (d) PANi/c-SiO\(_2\) composite and (e) PANi/a-SiO\(_2\) composite. It appears that PANi morphology (Fig. 2 (a)) shows the nanometer size, and the particles form a large agglomeration and the arrangement pattern of particles that form cavities between neatly arranged particles forming a particular pattern (as a polymer material). This is different for amorphous silica and crystalline silica morphology (Fig. 2 (b) and Fig.2 (c)), thus affecting its composite microstructure; as shown in Fig. 2 (d): PANi/c-SiO\(_2\) composite profiles and Fig. 2 (e) PANi/a-SiO\(_2\) composite profiles. Morphologi of the PANi/c-SiO\(_2\) appears to be more densely formed than composite particles of PANi/a-SiO\(_2\); on the surface part of the PANi/a-SiO\(_2\) particles there are polymer fibers that exhibit irregular composite tears and ductile bonds. Instead differs in small composite PANi/c-SiO\(_2\) composite pieces which have a uniform shape indicating a strong or brittle bond due to the filler crystal phase [10,19,23].
Figure 2. Morphology of: (a) PANi, (b) a-SiO$_2$, (c) c-SiO$_2$, (d) PANi/c-SiO$_2$, and (e) PANi/a-SiO$_2$
4. Conclusion

From the results of functional group vibration analysis with FTIR it is concluded that the composite PANi/SiO\textsubscript{2} both with amorphous and crystalline NPS fillers prepared by in-situ polymerization method have the same group vibration pattern; there is a difference in the strength of vibration (% transmittance), which is influenced by the filler particle phase, PANi/c-SiO\textsubscript{2} is stronger than PANi/ a-SiO\textsubscript{2} (95% : 5% sample). And microstructure (SEM result); there are significant differences between composite PANi/a-SiO\textsubscript{2} and PANi/c-SiO\textsubscript{2}, such as size, shape and cracks profile (ductile and brittle) and particle density.

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