INFLUENCE OF NANO ALPHA ALUMINUM OXIDE (α-AL₂O₃) ON THERMAL PROPERTIES OF NANO INSULATION COATING.

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Thermal insulation coatings are a class which begins to attract more focus and priority in recent researches because of their importance and their numerous applications in different civil and industrial fields. In this research, the effect of nano alpha aluminum oxide (α-Al₂O₃) on the thermal insulation of polymer based paint was investigated. The different weight fractions of nano aluminum oxide (2%, 3%, 4%, and 5% wt. of polymer weight) were added to the formulation which contained nano titanium dioxide and nano calcium carbonate and poly vinyl acetate polymer solution. Dip coating technique was used to coat all samples. The highest increase in insulation value (R-value) was recorded for 4% sample where its improvement percentage reached to 24.42% compared with the sample which was contained no nano aluminum oxide addition while the other samples showed varied values. The microscopic images showed that 4% sample has well dispersed than others. The Knudsen diffusion effect is the proposed mechanism explaining the insulation improvement.

Introduction:

Green Building is one of the most urgent environmental issues of our time. Buildings are responsible for 40 percent of the emissions responsible for global climate change and 42 percent of electricity in US [1]. So the present inclination and interest towards more sustainable "green" practices has forced a huge pressure on this material and energy utilization in the building environment for improvements and preservation.

Nanotechnology is widely regarded as one of the twenty-first century’s key technologies, and its economic importance is sharply on the rise. In the construction industry, nanomaterials has potentials that are already usable today, especially the functional characteristics such as increased tensile strength, self-cleaning capacity, fire resistance, and additives based on nano materials make common materials lighter, more permeable, and more resistant to wear. Nano-materials are also considered extremely useful for roofs and facades in the built environment. They also expand design possibilities for interior and exterior rooms and spaces. [2].

Nano-materials are additionally considered to a great degree valuable for roofs and frontispieces in the construction environment. They likewise extend plan potential outcomes for inside and outside rooms and spaces. Nano–insulating materials open up new potential outcomes for ecologically oriented sustainable infrastructure development. It has been exhibited that nanotechnology has fabricated products with numerous unique properties which could fundamentally give solutions current development issues and may change the necessity and organization of building process.

With the huge development in nanotechnology techniques, the doors were opened widely to develop the paints and coatings. Nanotechnology is regarded as one of the key technologies of the future in nano coating [3]. As a result,
new types of coating with new functions began to be synthesized. These new types were called functional coatings. The term “functional coatings” describes systems which possess, new an additional functionality besides the classical properties of a coating (i.e., decoration and protection) are added and in most cases it is a combination of these purposes. [4].

Functional coatings should frequently fulfill extra prerequisites; for instance, nonstick, cookware coatings which must be resistant to scratching and thermal impacts. Typical expectations of functional coatings include: durability, reproducibility, simple application and cost adequacy, customized surface morphology, environmental friendliness. In this manner functional coatings can be classified a few sorts relying upon their functional qualities. Functional coatings perform by methods of physical, chemical, mechanical, thermal properties. Chemically active functional coatings perform their activities either at film–substrate interfaces as it is existed in anticorrosive coatings, or in the bulk of the film like fire-retardant or intumescent coatings, while antibacterial or self-cleaning coating is an example of air–film interfaces.

This additional functionality may be diverse, and depend upon the actual application of a coated substrate. Typical examples of functional coatings are self-cleaning [5, 6], easy-to clean (anti-graffiti) [7], antifouling [8], soft feel [9], antibacterial [10, 11] and anti-corrosive [12, 13].

**Nano- materials in Coatings industry:**
Nano-particles are generally considered to be a number of atoms or molecules bonded together with radius of 100nm. A cluster of one nanometer radius has approximately 25 atoms, but most of them are on the surface of the cluster [14].

The appearance and appliance of nanomaterials conveys new chances to the coating industry. It is a clear that addition nano-materials to the coatings enhances the properties of the traditional coatings and produces new multi-functional coatings because of their tiny particle size.

In typical nanomaterials, the majority of the atoms located on the surface of the particles, whereas they are located in the bulk of conventional materials. Thus the intrinsic properties if nanomaterials are different from conventional materials since the majority of atoms are in different environments, since the majority of atoms are in different environments. Nanomaterials represent almost the ultimate in increasing surface area [15].

Nanoscale materials gives an obviously better solution in building insulating because of their high surface-to-volume proportion which empower them to trap vast measure of air with in a slim layer of material which prompts increment protecting capacity. The product item extend on insulation varies among paints, coatings, thin films or inflexible boards.

**Dip coating technique:**
Various techniques are used in coating fields like brushing, spraying, flow coating, spin coating and dip coating beside other techniques. Among of these methods, Dip coating technique is a suitable one to use because of its easiness, simplicity and it can be used to coat large and complex shapes of objects. So, this method was used in this paper.

Dip coating techniques can be described as a process where the substrate to be coated is immersed in the liquid or coating and then withdrawn with a controlled speed under controlled temperature and atmospheric conditions. Coating thickness increases with a faster withdrawal speed. Figure 1 shows the steps of dip coating process [16].
The speedier the withdrawal speed the all the more covering suspension is pulled up onto the substrate surface because there is no time for the suspension to stream down to the coating pool. Amid sol-gel dip coating, the covering suspension is quickly focused on the surface of the substrate by gravitational draining with related evaporation and condensation reactions.

It is noted the thermal functional coating researches are still fewer than what are existed for other functional coatings. So, in this research, the thermal insulation nano coating is synthesized and effect of nano alpha aluminum oxide ($\alpha$-$\text{Al}_2\text{O}_3$) is detected via measuring thermal conductivity of different loadings of nano alpha aluminum oxide ($\alpha$-$\text{Al}_2\text{O}_3$) which are added to coating formulations and their surfaces is investigated using optical microscopic methods.

**Material and Methods:**

The coating is consisted of amixture of materials including resin, solvent, pigment and additives as following:

A. Nano Aluminum oxide ($\alpha$-$\text{Al}_2\text{O}_3$), Nano Titanium dioxide ($\text{TiO}_2$) and Nano Calcium Carbonate ($\text{CaCO}_3$): properties are listed in Table 1

### Table 1: Physical properties of additives.

| Material              | Aluminum oxide | Calcium carbonate | Titanium dioxide |
|-----------------------|----------------|-------------------|------------------|
| Function              | Thermal effect | Thickener         | Pigment          |
| Chemical structure    | $\text{Al}_2\text{O}_3$ | $\text{CaCO}_3$ | $\text{TiO}_2$ |
| Phase                 | Alpha          | -                 | Anatase          |
| Crystal system        | Rhombohedral   | Cubic             | Tetragonal       |
| Particle size         | $< 50 \text{ nm}$ | $< 50 \text{ nm}$ | $< 50 \text{ nm}$ |
| Purity                | 99.8%          | 99.7%             | 99.8%            |
| Color                 | White powder   | White powder      | White powder     |
| Manufacturer          | Hongwunanometer company /China |

The crystal system and phase were characterized using XRD diffraction (XRD6000 – Shimadzu – Japan –Cu target, Cu target – 1.54060 Å$^2$). The results showed that $\text{Al}_2\text{O}_3$ was identical with values of ICDD (PDF #10-0173). The Figure 2 clarified the XRD pattern of corundum ($\alpha$-$\text{Al}_2\text{O}_3$) with rhombohedral crystal system.
B. Poly vinyl acetate (PVAc) solution: the specifications of Poly Vinyl Acetate which was used as polymer base of nano coating are listed in Table 2

**Table 2:- Physical properties of Poly Vinyl Acetate solution.**

| Chemical structure | Chemical structure | Surface dryness time | Complete dryness |
|--------------------|--------------------|----------------------|------------------|
| {\( (C_2H_3O_2)_n \)} | 1.2 ± 3% g/cm\(^3\) | 20-30 min | 1-2 hr |
| Density           | Solid ratio        |                     | Manufacturer     |
|                   | (48.5 ± 2%)        |                     | China            |

**Preparation method:-**
The preparation method of nano coating can be summarized as following steps:
1. Different weight fractions of materials were mixed as shownin Table (3)

**Table 3:-Nano coating formulations.**

| Sample code | PVAc (g) | Nano CaCO\(_3\) (g) | Nano TiO\(_2\) (g) | Nano Al\(_2\)O\(_3\) (g) | Al\(_2\)O\(_3\)/ PVAc(wt.%) |
|-------------|----------|---------------------|-------------------|--------------------------|------------------------|
| SAP 0       | 50       | 2.5                 | 0.5               | -                        | 0                      |
| SAP1        | 50       | 2.5                 | 0.5               | 1                        | 2                      |
| SAP2        | 50       | 2.5                 | 0.5               | 1.5                      | 3                      |
| SAP3        | 50       | 2.5                 | 0.5               | 2                        | 4                      |
| SAP4        | 50       | 2.5                 | 0.5               | 2.5                      | 5                      |

2. All materials in table 3 were added gradually to the polymer solution. Every material was added and mixed with PVAc solution using a mechanical stirrer (Daihan Scientific 1500 rpm / South Korea) for 30 minutes before adding the other material

3. Dip Coating method was used to coat al samples. The sample substrate (glass slide) was submerged vertically in coating solution for 15 seconds and then it retracted vertically at suitable speed. The thickness was adjusted to be (1 mm) for all samples and they left to dry at ambient conditions for 24 hours before testing. Figure 3 shows the prepared samples on glass slides.
Tests:
- Microscopic test: the test was done by using light microscope (ML-7000/ MEIJI TECHNO /JAPAN)
- Thermal conductivity: the tests were done via the thermal conductivity meter: (C-ThermTCi Thermal Analyzer, SETARAM company, France)

Result and Discussion:

Thermal conductivity test:
Table 4 is shown the results of thermal conductivity and effusivity of prepared samples:

| Samplecode | Effusivity(W/s\(^{1/2}\)/m\(^2\)k) | Thermal conductivity(W/M.K) |
|------------|-----------------------------------|-----------------------------|
| SAP 0      | 1114.4                            | 0.749                       |
| SAP1       | 996.0                             | 0.622                       |
| SAP2       | 984.145                           | 0.615                       |
| SAP3       | 976.9                             | 0.602                       |
| SAP4       | 1312.5                            | 0.976                       |

R-Value (thermal insulation) is calculated for prepared samples according to the equation 1:

\[ R\text{-Value} = \frac{L}{k} \]  

Where: \( L \) = thickness of coating (1 mm),
\( k \) = thermal conductivity

Table 5: R-values of prepared samples.

| Sample code | SAP0 \times \times 10^3 | SAP1 \times \times 10^3 | SAP2 \times \times 10^3 | SAP3 \times \times 10^3 | SAP4 \times \times 10^3 |
|-------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Thermal insulation (m² K/W) | 1.335 | 1.601 | 1.626 | 1.661 | 1.024 |
| Insulation Improvement ( % ) | - | 19.92 | 21.79 | 24.42 | - 31.1 |
Figure 4: R-value of prepared samples.

Table 5 and Fig. 4 in above shows R-values for all samples. The assessment of the results comparing to sample SAP0 (without α-Al₂O₃) shows varied values of R-value (according to addition amount). As it is noted, The improvement of sample insulation (SAP3) is highest (24.42%) among all samples. In return, the lowest R-value records for sample (SAP4).

The reason of this increasing in R-value can be explained depending on Knudsen effect theory and porosity of alpha alumina as following:

- Nano scale effects of alumina can significantly reduce the heat transfer caused by conduction. Heat transfer by conduction is the transport of heat by microscopic diffusion and collision of particles or quasi-particles (molecule, phonon, electron etc.) within a body due to a temperature gradient. When the linear dimensions of the medium (PVAc) are comparable to the mean free path of the particles, the heat transport from particle to particle is inhibited. The particle will collide with the pore wall with increasing probability and the heat conduction due to intermolecular collision will be less and less probable as the pore size becomes smaller. This is often referred to as the Knudsen effect, or Knudsen diffusion [18].

- The nano alumina is a porous material and it has high surface area and nano pores in its structure so the air will be trapped in these pores leading to improve the insulation properties of the coating.

Whereas, the thermal insulation of SAP4 decreased drastically when the ratio of nano alumina increased to 5%wt. because of the thermal conductivity improvement as a result of aggregate the particle of nano alumina with each other and with other nano ingredients (nano TiO₂, nano CaCO₃) in clusters which contribute to enhance the thermal conductivity of nano systems, according to Evans and his team conclusions which reveal the thermal conductivity enhancement is mainly attributed to the aggregation and cluster of nano particles which enhances the ability of heat to move rapidly along the backbone of the particles cluster (The linear chains which span the whole cluster). Due to its connectivity, the backbone is also expected to play a crucial role in thermal conductivity. This increase is mainly caused by the increased size of the backbone that promotes rapid conduction across the cluster. This is associated with the fact that particles act as constant temperature regions and the resistance to the heat flow comes only from the matrix. However, aggregation of the particles into clusters is expected to utilize the high particle conductivity more effectively [19].

Optical Microscopy test: -
The microscopic test was done to investigate therm morphology of the surfaces of the samples. The images of the samples (Figure 5) clarify the surfaces. The key to getting good insulation paints is the well distribution of fillers in
the polymer matrix to fulfil the conditions of Knudsen rule. The study of optical microscope images show that image of SAP3 well dispersed fillers and that lead to get high insulation result. On the contrary, the other images have varied dispersion degree and homogeneity. As same time, image of sample (SAP4) shows the clusters and agglomerations of particles in matrix.

![Prepared sample [SAP0]](image01)
![Prepared sample [SAP1]](image02)
![Prepared sample [SAP2]](image03)
![Prepared sample [SAP3]](image04)
![Prepared sample [SAP4]](image05)

**Figure 5:** optical microscopic images of prepared samples
Conclusion:
The results are shown that nano aluminum oxide additions to paints contribute in improving the insulation property of paints with varied values. The highest improvement of the insulation was recorded for the sample which was contained 4% of the nano aluminum oxide among all the samples. The thermal insulation (R-value) of prepared paints increased 24.42 % compared with the sample without alumina addition. Depending on the results of this research, thermal insulation paints open new fields to use this kind of coating in insulation applications.

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