Development on advanced electrophoretic deposition system for fabrication and processing of irradiated hybrid nanocomposites

Mohd Roslie Ali1,a), Meor Yahaya Razali1, Mohd Hamzah Harun1, Ahmad Zuhdi Mohd On1, Muhammad Hazim Muhd Sayuti1, Khairul Azhar Abdul Halim1

1Radiation Technology Division, Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor, Malaysia.

a)roslie@nuclearmalaysia.gov.my

Abstract. Electrophoretic deposition (EPD) is attracting increasing interest as a materials processing technique for a wide range of technical applications. This technique enables the production of unique microstructures and nanostructures as well as novel and complex material combinations such as hybrid nanocomposites, in a variety of macroscopic shapes, dimensions and arrangements starting from micron-sized or nanosized particles. In the standard EPD process (lab scale), two electrodes, the working electrode (substrate material) and the counter electrode are immersed in a suspension. In pilot scale, the fully automated system consists suspension compartment with ultrasonic transducer, electrodes in-line system, programmable AC/DC power supply, washing system, drying/ annealing system and others. The advantages of EPD are rather simple equipment, the flexibility in substrate shape/dimension and coating materials choice as well as the ability to easily control the homogeneity and thickness of the coatings. Pilot scale deposition facilities or the advanced EPD system, involves semi-automatic operation with accurate deposit thickness control. This promising technique is a better choice than other techniques which are more expensive, less efficient and harmful to environment. The hybrid nanocomposites have been proven to exhibit superior properties than the conventional materials. To make full use of the properties derived from particles, it is important to control the arrangement of particles with high packing density in hybrid nanocomposites. The Ultrasonic irradiation assisted in this system has been found to enable desired particle arrangement and packing density with various shapes. Besides, with the implementation of Gamma irradiation (Pretreatment) as replacement for chemical treatment and EB irradiation for enhancement of conductivity and uniformity of the coatings (Post treatment) can distribute efficiently. It is expected that the system is enable to be employed in variety functions and applications. This paper will discuss the development of the system, the advantages and the relevancy of this system in variety applications.

1. Introduction

Nanocomposite is a composite for which at least one of the dimensions of the dispersed phase is in the nano-meter range. Even if the term “nanomaterials” or “nanocomposites” appeared at the end of the decade eighties, the practical use of this type of materials is much older. The tremendous potential filler matrix interface, combined with the same size of the components of the dispersed
phase, makes this type of nano-composites are very attractive, since they are expected to require much lesser amounts of filler to obtain similar or even better levels of performance (with regards to mechanical, thermal and electrical properties)

One very promising manipulation technique in manipulation and fabrication of nanocomposite is electrophoretic deposition (EPD), which has recently been reviewed in the context of nanocomposites. EPD fundamentally is a combination of two processes, electrophoresis and deposition. In the first step, materials (particles) were suspended in a liquid are forced to move towards an electrode by applying an electric field. In the second step, the particles are collected at the electrode and formed a coherent deposit. EPD has a number of advantages when using particulate suspensions to generate films and coatings. The attraction of this method lies in its simplicity. EPD is a cost-effective method usually requiring simple equipment and yet it offers the possibility of forming monolithic or composite coatings with complex shapes and surface patterns. In addition, EPD requires only short processing time. All of these advantages can be exploited for forming films and coatings of nanomaterials.

Normally the multilayered films or coatings prepared by EPD are just in laboratory scale. It is involved with complicated procedures including inserting/remaining electrode substrates into/from EPD bath suspensions, electric field applying (output voltage), washing and drying system are manually controlled. Therefore, the multilayered films or coatings obtained from manual or batch process are nearly unrepeatable because of wide range of the procedures.

EPD is an important technique usually for colloidal or microstructures coating and deposition. It has the advantages of rapid, large-area deposition of films with high packing density and controllable thickness at a low-cost. It uses applied electric fields, to move electrically charged colloids or particles in suspension towards electrodes and finally to form films deposition it. The fabrication of multilayered coatings is significant technique in the producing energy devices for solar application. There also many targeted application rising up such biomedical, automotive industry, environment and military.

The conventional techniques like dip coating and painting for fabrication and processing of composites have drawbacks especially inability to obtain large area with uniform quality and limited to planar surface, due to difficulties in controlling the microstructures and the thickness of the coatings[1]. Furthermore, current techniques available in market are more expensive and consume more energy which requires specialized equipment. The highly demands for new simple system is more preferable.

In this paper, we proposed to introduce the EPD system which can be developed for fabrication and processing of hybrid nanocomposites. The review of this system includes an overview of building up the system of EPD from lab method to fully utilized system in pilot plant. The details on key parameters, benefits and also the potential of this system will be discussed.

2. Experimental

2.1. Concept of EPD System
Electrophoretic deposition (EPD) is a two-step process for depositing coatings from suspended particles and polymer molecules. In the EPD process, the substrate itself is immersed as an electrode in a suspension of fine particles. Basically, any electrically conductive substrate is applicable for EPD. EPD requires the homogeneous dispersion of charged particles in a suspension medium. The suspension should be stable over the deposition period to prevent uncontrolled microstructure of the coatings. In the standard lab process, two electrodes, the working electrode (substrate/targeted materials) and the counter electrode are immersed in the suspension. When applying an electric field, the particles move towards the oppositely charged substrate material, where in the next step they deposit to form coatings.

Figure 1 shows the schematic diagram of EPD and overall setup of the EPD in lab scale. Our purpose is to upgrade the system in pilot plant in order to make them full utilized in fabrication and processing of Hybrid Nanocomposites. The traditional or conventional of electrophoretic in the lab
will be enhanced and the development of a new system in the pilot plant will be setup systematically. In the pilot plant, the system of EPD will be assisted with Ultrasonic irradiation as pre-treatment and \textit{in-situ} technique. The sequences of this system will be featured in combination of multi components.

![Schematic of EPD](image1)

**Figure 1.** Setup of the electrophoretic deposition in lab scale

Points of Understanding regarding EPD as follows:

i) All composites / colloidal particles that can be used to form stable suspensions and that can carry a charge can be used in EPD such as polymers, pigments, dyes, ceramics and metals

ii) It differs from electrolytic in several ways (No redox reaction occurs)

iii) The types of EPD depend on which electrode the deposition occurs (Cathodic or Anodic EPD)

iv) The deposits / coatings are not necessarily electrically conductive

v) Useful for applying materials to any electrically conductive surface

2.2 System components

Figure 2 shows the designated of sequences of EPD system in a pilot scale. In these batches system, there are four (4) functions:

i) Deposition / Coating: In this function, EPD process can be operated under variable conditions. For instance, the deposition time, the voltage applied or output potential. This \textit{in-situ} system also can be synchronizing with ultrasonic irradiation by manipulating the amplitude of the vibration applied.

ii) Washing: the fabricated materials can be repeatedly dipped or immersed into washing solvent and then withdrawn until they are well-cleaned. Any solvent can be filled in and drained out by controlling the inlet and outlet of the washing container.

iii) Drying: During this process, the fabricated materials can be dried in the oven with temperature controlled or blown with heated air. The blower also can be installed in the container after the washing process.

iv) EB irradiation: This post treatment can be applied separately after the fabricated materials have been fully deposited, cleaned and dried. The thickness of the affected material can be varied by changing the beam power. The purpose of Electron-Beam irradiation treatment is to densify the electrophoretic deposit and to make sure it more adherent to substrates. Thus it will assist in uniformity of the deposition or the coatings
2.3. Preparation of Hybrid Nanocomposites

There are many types of method that could be used to prepare the hybrid nanocomposites. In this study, the combination of the polymers and other materials will be chosen based on their effectiveness and targeted applications. For example, conductive polymer like polypyrrole can be combined with carbon nanotubes (CNT) or graphene and other advanced materials like titanium dioxide (TiO2) to form nanocomposites. The manipulation of ratios of the mixtures is vital in this stage. The process can be achieved by conventional polymerization or by electropolymerization. As pre-treatment, functionalization by acid reflux or gamma irradiation can be used for achieving the better dispersion in suspension. The stability of the suspension can be achieved by assisting the ultrasonic irradiation as pre-treatment before EPD technique.

3. Discussions

3.1. What happens in EPD process?

As in Figure 3, after migration of the charged particles from the bulk to the electrode of the opposite charged electrode, the deposition occurs through the double layer (lyosphere) distortion and thinning followed by coagulation of the particles on the electrode. When the charged particles that is surrounded by the diffuse double layer is subjected to an electric field, it undergoes a distortion and becomes thinner ahead and wider/thicker behind. During the migration of the charged particles, ions of similar charge will move in the same direction of the particles and can react with the counter ions accompanying the charged particle. The latter induces a thinning of the double layer of the particles. Because the double layer of the particles is now thinner, it can easily approach other particles with also a thinner double layer and, if the contact is close enough to favor Van der Waals attractive forces domination, hence the deposition occurs.

Conventionally for this technique, the substrates or targeted materials was needed to be electrically conducted. However, the latest research that was newly investigated, found that the EPD can be applied even on non-conducting substrates or targeted materials. This can happen by isolating the influence of porosity effect.
Figure 3. The mechanism of EPD.

The mechanism of EPD involves charged particles in a suspension being deposited onto an electrode under the influence of an applied electric field. Two groups of parameters or factors determine the characteristics of this process; (i) those related to the suspension (Figure 4) and, (ii) those related to the process including the physical parameters such as the electrical nature of the electrodes, the electrical conditions (voltage/intensity relationship, deposition time, and others).

Figure 4. The factors influencing EPD related to suspension.

EPD mainly contains aqueous, organic polar solvents and nonpolar solvents. In general, low voltage range below 20V applicable to aqueous solvents. For medium range of voltage below 100V suitable for polar solvents. As for nonpolar solvents, it requires voltages above 100V. Utilizing nonpolar solvents is preferable for the uniform deposition of materials, but the required high voltage is unfavorable for the chemical stability of the EPD system. For aqueous solvents or electrolytes, even though with a low voltage, bubbles are readily formed due to the production of hydrogen and
oxygen by water electrolysis, which leads to low-quality EPD deposition or coatings. In addition, highly active hydrogen and oxygen atoms also give rise to side reactions in EPD. In particular, the applied voltage impacts substantially the morphology of EPD materials, in this case, hybrid nanocomposites, as well as the performance of the fabricated materials. Therefore, polar solvents like ethanol and acetone are widely used in EPD.

3.2. Why use ultrasonic irradiation in EPD?
The preparation of stable suspension/dispersion of hybrid nanocomposites in suitable liquids/solvents necessarily prerequisite for successful deposition by EPD. The individual particles are held together by attraction forces of various physical and chemical nature, including van der Waals forces and liquid surface tension. This effect is stronger for higher viscosity liquids, such as polymers or resins. The attraction forces must be overcome in order to deagglomerate and disperse the particles into liquid media. The application of mechanical stress in ultrasonication of the media resulting in alternating high pressure (compression) and low pressure (rarefaction) cycles on the attracting electrostatic forces (Figure 5). Hence the pressure between the particles will separate and make effective means for dispersing and deagglomeration especially in pilot plant system of EPD.

![Figure 5. The particles condition before and after ultrasonication.](image)

3.3. Electron-Beam Irradiation (Ionizing) Effect on EPD Coatings
As in Figure 6 on EB Treatment, the reflectivity by the irradiated material is lower compared to laser energy, therefore the beam efficiency is higher. The thickness of affected material can be varied by changing the beam power. This alternative method was successfully used to densify the electrophoretic deposits/coatings and to make it more adherent to substrates or targeted materials. Thus it will assist in uniformity of the coatings.
3.4. Techniques for characterization of Deposited Hybrid Nanocomposites

There were several experimental techniques used for the characterization of deposited hybrid nanocomposites on the substrates or targeted materials.

3.4.1. Characterization of deposition suspension. The stability of the suspensions can be analyzed by Particle Size analyzer and Zeta Potential. The suspensions can be compare between suspensions with and without ultrasonic irradiation applied. The suspensions were ultrasonically treated to ensure its homogeneous distribution before test. Other characterization such as Transmission electron microscope (TEM) can be used to analyze composition of hybrid nanocomposites which synthesized from electropolymerization and functionalization.

3.4.2. Surface morphology and microstructure analysis. The deposits or coating morphology can be observed by Scanning Electron Microscope (SEM). The microscopic Fourier Transform Infrared Analysis (FTIR) and Raman Spectrometer can be utilized to investigate the functional groups of the deposits or coatings. For topography of hybrid nanocomposites surfaces and interfaces, or the surface roughness, can be analyze by Atomic Force Microscope (AFM). The thermal stability of nanocomposites can be evaluated by thermo gravimetric analysis (TGA). As for Differential Scanning Calorimeter (DSC), the nature of crystallization in matrix of the nanocomposites can be studied. X-Ray Diffraction (XRD) can be used to ensure the availability of the deposition and coatings on targeted materials.

Figure 7 and 8 show the images of the MWCNT films deposited on Aluminum plate/substrate by Electrophoretic deposition (EPD) technique and the Scanning Electron Microscope (SEM) micrographs. The SEM micrographs indicate that some cracks in the film surface which are attributed to the tension stress induced by the mismatch of the thermal expansion coefficient between deposition layer and substrate [6]. When EPD was carried out at the optimal parameters, very homogeneous MWCNTs deposits were obtained, about 2µm thick MWCNT coatings were produced.
Figure 7. Image of deposited of MWCNTs film onto the Aluminum plate/substrate.

Figure 8. SEM micrographs of surface morphology of MWCNTs film onto the Al-plate, (inset: cross-sectional image of MWCNT films, scale bar: 500 nm).

3.5. Potential applications of EPD system
In recent years, there has been a rising interest in nano and micro-structured materials because they usually exhibit novel and improved properties suitable for various applications. Compared to other deposition and coating process such as grafting, lithography, self-assembly, dip-coating, spin coating and the advanced technique like CVD and PVD, EPD technique offers the advantage of being versatile, cost saving and more importantly, allows deposition of high rates of particles in a controlled structural manner.

The applications of deposits or coatings by EPD can be applied in advanced ceramic materials, coatings for thin and thick films, multilayered composites, functionally graded materials, hybrid materials and nanotechnology. These fabrication and coatings can cover in many potential applications such as shielding for electromagnetic radiation (Power plants, reactors and telecommunication). In reinforcement composites, this technique can have covered materials for construction, automotive and aerospace. EPD under modulated electric fields can offer new application perspectives in biotechnology such as implants, prostheses, drug delivery and medical devices.
EPD is an automated process, a variety of parameters such as voltage, frequency, concentration of dispersed species and deposition time can be controlled to yield a better response under the optimized conditions. With regards to this, large number of fabricated microstructures with improved characteristics have recently been designed and manufactured. In energy and electronic devices, EPD can be future prospect in solar cell technology, energy storage, fuel cells, super capacitor and super electrodes devices.

In environmental field, EPD can be developing for building up the system of desalination separation membranes, air purification, wastewater treatment and the removal of ionic and heavy metals. There also electrochemical system which have been done for water purifications and the development of adsorbents from polymer nanocomposites by this technique. Others promising applications of this versatile technique can be gained in painting technologies, alloy metals processing, corrosion protection and as tools for supporting another processing technique.

4. Conclusions
The investigation confirms that Electrophoretic deposition (EPD) represents a very convenient processing technique for the deposition of hybrid nanocomposites onto various substrates and targeted materials that may be relevant to a variety of applications. Due to high efficiency, scaling up capability, cost effectiveness and easily control in assembly, EPD system exhibits advantages in realizing nanostructured and composite films or coatings for many applications such as energy conversion, fuel cells, biomedical devices, environment, automotive and aerospace. The deposited materials from hybrid nanocomposites exhibited excellent macroscopic homogeneity and uniformity of thickness throughout. A further improvement in the various properties of the conductive or nonconductive substrates, such as its electrical conductivity and optical transmission, should be possible by enhancing the degree of dispersion of the hybrid composites in the well stable suspension. The fully utilized and automated EPD system can promising us future advanced applications in many aspects.

5. References
[1] Azuma S, Yamada H, Kawamura G, Muto H, Mizushima T and Matsuda 2017 A Development of multilayer coating system based on electrophoretic deposition process. J. of the Ceramic Soc. of Japan 125(4) p 317-321.
[2] Bhardwaj S, Pal A, Chatterjee K, Chowdhury P, Saha S, Barman A, Rana H, Sharma G D, Biswas S 2017 Electrophoretic deposition of plasmonic nanocomposite for the fabrication of dye-sensitized solar cells. Indian J. of Pure and Appl. Phys. 55 p 73-80
[3] Jiang J, Xu C, Su Y, Guo Q, Liu F, Deng C, Yao X and Zhou L 2016 Influence of carbon nanotube coatings on carbon fiber by ultrasonically assisted electrophoretic deposition on its composite interfacial property. Polymers 8 p 302.
[4] Wang C, Li, Sun S, Li X, Zhao F, Jiang B, Huang Y 2016 Electrophoretic deposition of graphene oxide on continuous carbon fibers for reinforcement of both tensile and interfacial strength. Composites Sci. and Tech. 135 46-53.
[5] Shi Y Y, Li M, Liu Q, Jia Z J, Xu XC, Cheng Y, Zheng Y F 2016 Electrophoretic deposition of graphene oxide reinforced chitosan-hydroxyapatite nanocomposite coatings on Ti substrate. J Mater Sci: Mater Med 27 p 48.
[6] Seuss S, Lehmann M, Boccaccini A R 2014 Alternating Current Electrophoretic Deposition of Antibacterial Bioactive Glass-Chitosan Composite Coatings Int. J. Mol. Sci. 15 p 12231-12242.
[7] Shi K, Zhitomirsky I 2013 Electrophoretic nanotechnology of graphene-carbon nanotube and graphene-polyprrole nanofiber composites for electrochemical supercapacitors J. of Colloid and Interface Sci. 407 p 474-481
[8] Ammam M 2012 Electrophoretic deposition under modulated electric fields: a review. RSC Advances 2 p 7633-7646.
[9] Cho J, Konopka K, Rozniatowski K, Garcia-Lecina E, Shaffer M S P, Boccaccini A R 2009 Characterization of carbon nanotube films deposited by electrophoretic deposition. Carbon 47 p 58-67.
[10] Wang S C, Huang B C 2008 Field emission properties of Ag/SiO2/carbon nanotube films by pulsed voltage co-electrophoretic deposition. Thin Solid Films 517 p 1245-1250.

[11] Jung S M, Jung Y, Suh J S 2008 Horizontally aligned carbon nanotube field emitters fabricated on ITO glass substrates. Carbon 46 p 1973-1977.

[12] Havel M, Behler K, Korneva G, Gogotsi Y 2008 Transparent Thin Films of Multiwalled Carbon Nanotubes Self-Assembled on Polyamide 11 Nanofibers. Adv. Funct. Mater. 18 p 2322-2327

[13] Besra L, Liu M 2007 A review on fundamentals and applications of electrophoretic deposition (EPD). Progress in Materials Science 52 p 1-61.

[14] Besra L, Compson C, Liu M 2007 Electrophoretic deposition on non-conducting substrates: The case of YSZ film on NiO-YSZ composite substrates for solid oxide fuel cell application. J. of Power Sources 173 p 130-136.

[15] Chow Winnie W Y, Wong M K, Li W J, Wong K W 2007 Rapid fabrication of CNT sensors using electro-chemical deposition of functionalized CNTs. Proc. of the 2nd IEEE Int.1 Conf. on Nano/Micro Eng. and Molecular Sys.

[16] Boccaccini A R, Cho J, Roether J A, Thomas B J C, Minay E J, Shaffer Milo S P 2006 Electrophoretic deposition of carbon nanotubes. Carbon 44 p 3149-3160.

[17] Moniruzzaman M and Winey K I 2006 Polymer Nanocomposites Containing Carbon Nanotubes. Macromolecules 39 p 5194-5205

[18] Amerio E, Sanguermino M, Malucelli G, Priola A, Voit B 2005 Preparation and characterization of hybrid nanocomposite coatings by photopolymerization and sol-gel process. Polymer 46 p 11241-11246.

[19] Kamat P V, Thomas K G, Barazzouk S, Girishkumar G, Vinodgopal K, Meisel D 2004 Self-assembled linear bundles of single wall carbon nanotubes and their alignment and deposition as a film in a dc field. Jacs Art.

[20] Kamada K, Mukai M, Yasumichi M 2003 Electrophoretic deposition assisted by soluble anode. Materials Letters 57 p 2348-2351.

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