

A REVIEW OF NANO-FILLERS EFFECTS ON INDUSTRIAL POLYMERS AND THEIR CHARACTERISTICS

A.THABET, Y. A. MOBARAK, and M. BAKRY

Aswan, Nanotechnology Research Centre NTRC, High Institute of Energy, South Valley University, Aswan, Egypt

(Received December 24, 2010 Accepted March 28, 2011)

This paper reviews recent advances in the field of developing industrial polymers by nanocomposites materials. The discussed materials have been attracted in both academic and industrial attention because they exhibit dramatic improvement in properties at selected low filler contents. Herein, the types and forms of industrial polymer, structure, and properties of polymer-nanocomposites are discussed. Traditionally, polymeric materials have been filled with synthetic or natural inorganic compounds in order to improve their properties, or simply to reduce cost. Also, this paper investigates various factors affecting on the electrical properties of the polymers insulating materials, and the optimum properties for the novel nanoscience materials. Finally, this paper discusses the comparison between selected nanofillers on polymers, and production procedures formatting polymer nanocomposite. Polymeric materials have become an alternative choice for electrical and electronics applications. These applications require multi-functionality in a single material which is not usually found in a typical polymer. An economical way to fabricate multi-functional materials is to mix polymer with other materials. In the nanocomposite systems where the fillers typically have nano-meter-scale dimensions, the property improvement in such systems normally comes with tradeoffs.

KEYWORDS: *Polymers, Nano-Filler, Selected Polymer, Materials*

1- INTRODUCTION

Polymers are generally known to be good insulating materials due to their stable physical and chemical properties [1-10]. Both the mechanical and electrical properties of polymers, however, can be further improved or modified with the addition of inorganic fillers as demonstrated by increases in the mechanical strength of the composite and changes in the electrical conductivity. It is known that the composite properties can also change with the dispersion state, geometric shape, and surface quality of the filler particles as well as the particle size. For example, the effect of carbon black dispersion in polymer blends on the electrical conduction properties of the composite, and the dependence of electrical properties on the shape and distribution of the filler particles were reported [11-15]. Owing to the recent commercial availability of nanoparticles, the outlook for composite materials with new or modified physical properties became even brighter. Nanoscale fillers are different from bulk materials and conventional micron-size fillers due to their small size and corresponding increase in surface area. It is expected that the addition of nanoparticles into polymers

would lead to unprecedented ability to control the electrical properties of filled polymers [16-21].

Furthermore, nanocomposite materials with length scales smaller than 1 μm are becoming necessary as the size of modern electronic devices reach down to submicron scales. Therefore, understanding how to control the resistivity and permittivity of nano-filled polymer nanocomposites is an essential step toward the controlled engineering of nanocomposite materials in future electrical applications [22-30].

Lee and coworkers [7] reported a study on ABS/clay systems obtained by an emulsion technique while Wang and Hu [20] produced and characterized intercalated delaminated nanocomposites using direct melt intercalation. Stretz et al. [34] discussed the dispersion of clay particles in an ABS matrix comparing this system with a styrene-acrylonitrile (SAN) based nanocomposite, where it was observed that the ABS/MMT composite clay resides in the SAN phase of ABS and accumulates preferentially at the rubber particles surface. Pourabas and Raeesi [35] prepared an ABS/clay nanocomposite developing a solvent/ non-solvent method and working with different kinds of mixers while Jang and Wilkie [37] studied the effect of the clay on the thermal degradation behaviour of ABS [30-38].

2- BASIC DEFINITIONS

2.1 Nanoparticles

Nanofillers are generally categorized into three geometries i.e. equi-axial (particles), rod (fiber-like), and sheet. A significant advantage of small-sized particle is the high surface-to-volume ratio which is varied by the particle geometry. Properties of polymer nanocomposites can be tailored by type of nano-scale fillers used in the system. Many types of nanofillers are commercially available today. Clay or Montmorillonite (MMT) is one of the most studied in polymer nanocomposites. Other fillers include carbon, aluminum oxide, and silica. The following sub-sections describe examples of filler [39, 40].

2.2 Effects of Fillers

Traditionally, fillers were considered as additives, which, due to their unfavorable geometrical features, surface area or surface chemical composition, could only moderately change the characteristics of the polymer. Their major contribution was in lowering the cost of materials by replacing the more expensive polymer; other possible economic advantages were faster molding cycles as a result of increased thermal conductivity. Depending on the type of filler, other polymer properties could be affected; for example, melt viscosity could be significantly increased through the incorporation of fibrous materials. On the other hand, mold shrinkage and thermal expansion would be reduced, a common effect of most inorganic fillers [40-44].

2.3 Functional Fillers Classification and Types

The term filler is very broad and encompasses a very wide range of materials, fillers a variety of solid particulate materials (inorganic, organic). There is significant diversity in the chemical structures, forms, shapes, sizes, and inherent properties of the various compounds that are used as fillers. They are usually rigid materials, immiscible with

the matrix in both the molten and solid states. Fillers may be classified as inorganic or organic substances, and further subdivided according to chemical family, and function as shown in Tables 1&2. [45-51].

Table 1 Chemical Families of Fillers for Polymers

Chemical Family	Examples
Inorganic Oxides	Glass (Fibers, Spheres, Hollow spheres, flakes), MgO, SiO ₂ , Sb ₂ O ₃ ,
Hydroxides	Al(OH) ₃ , Mg(OH) ₂
Salts	CaCO ₃ , BaSO ₄ , CaSO ₄ , Phosphates
Silicates	Talc, Mica, Kaolin, Wollastonite, Montmorillonite, Nanoclay, Feldspar, Asbestos
Metals	Boron, Steel
Carbon – Graphite	Carbon fibers, Graphite fibers, and Flakes, Carbon nanotubes, Carbon black
Natural Polymers	Cellulose fibers, Wood flour and fibers, flax, cotton, sisal, starch
Synthetic Polymers	Polyamide, Polyester, Aramid, Polyvinyl alcohol fibers

Table 2: Fillers and their Functions

Primary Function	Examples of Fillers	Additional Functions	Examples of Fillers
Modification of Mechanical properties	High aspect ratio: glass fibers, mica, nanoclays, carbon nanotubes, carbon /graphite fibers, aramid/synthetic / natural fibers Low aspect ratio: Talc, CaCO ₃ , kaolin, wood, flour, glass, wollastonite, spheres	Control of Permeability	Reduced permeability: impermeable plate-like fillers: mica, talc, nanoclays, glass flakes Enhanced permeability: stress concentrators for inducing porosity: CaCO ₃ , dispersed polymers
Enhancement of fire retardancy	Hydrated fillers: Al(OH) ₃ , Mg(OH) ₂	Bioactivity	Bone regeneration: hydroxyapatite, tricalcium phosphate, silicate glasses
Modification of electrical and magnetic properties	Conductive, non-conductive, ferromagnetic: metals, carbon fibers and nanotubes, carbon black, mica	Degradability	Organic fillers: starch, cellulosic
Modification of surface properties	Antiblock, lubricating: silica, CaCO ₃ , PTFE, MoS ₂ , graphite	Radiation Absorption	Metal particles, lead oxide, leaded glass
Enhancement of processability	Thixotropic, anti-sag, thickeners, acid scavengers: colloidal silica, bentonite, hydrotalcite	Improved dimensional stability Modification of optical properties Control of damping	Isotropic shrinkage, reduced warpage: particulate fillers, glass beads, mica Nucleators, clarifiers, iridescent pigments: fine particulates, mica/pigment hybrids Flake fillers, glass, BaSO ₄

2.4 Modification of Mechanical Properties

Modification of mechanical properties and, in particular, the enhancement of modulus and strength is undoubtedly one of the most compelling reasons for incorporating functional fillers into polymers. Appropriate selection of a filler based on its size and shape, modulus and strength, and density is of paramount importance in order to establish its potential reinforcing capacity and to provide guidelines for its method of incorporation into the polymer. The data may be subject to variation, considering measurement difficulties, particularly for fillers of different origins. In particular, the strength values should be viewed with caution since they depend on the method of testing and the effects of flaws and edges [52-60]. Silicon and oxygen are common to all clay minerals, and the combination with other elements such as aluminum, magnesium, iron, sodium, calcium, and potassium, and the numerous ways in which the elements can be linked together make for a large number of configurations [61, 62].

3- CLAY FILLED POLYMERS

All other clays contain various impurities (other minerals) and it is these impurities that give the clays their particular characteristics and colors. Silica is the dominant constituent of clays, with alumina being essential as well. Table (3) [40] shows the selected mechanical properties of clay. Those data may be subject to variation considering measurement difficulties, particularly for clay of different origins. Nanoclays are relatively new commercial products and, as such, the cost/price structure has yet to be established. Although a variety of products appear to be available from the suppliers listed, the quantities being sold are small and reflect specialty and developmental pricing policies. The health and environmental issues for nano-clays specifically are minimal and manageable. Sister organically products have been used for many years in a host of industrial and consumer products. The perception that nano-clays are somehow different because of the prefix “nano” may be the problem. Nano-clays only become “nano” when they are placed in a host polymer matrix, whereupon they cannot be separated or distinguished from the bulk polymer and other constituents. Crystalline silica is a naturally occurring component that may be present in commercial alkyl quaternary ammonium bentonite when inhaled presents a health hazard to humans and is regulated to very low permissible exposure limits.

Polymer-clay nanocomposites represent an interesting topic in insulating materials manufacturing because of their promising properties which can be obtained with very low filler content. As well known, the performances improvement of these composites is realized when clay particles are accurately dispersed in the polymer matrix and intercalation between matrix macromolecules and clay lamellae exist.

Nanoclays, in addition to their primary function as high aspect ratio reinforcements, also have important additional functions such as thermal and barrier properties and synergistic flame retardancy. Some of the factors responsible for good performance in nanocomposites are: intercalation (surfactant & polymer); interfacial adhesion or wetting; exfoliation (dispersion and delaminating) [2-6].

Mechanical	Si/ Metric	Mechanical	Si/ Metric
-------------------	-------------------	-------------------	-------------------

Density	1.2 – 2.45g/cm ³	Shear Modulus	6.85 Gpa
Porosity	30 %	Bulk Modulus	20.9 Gpa
Flexural	2 -10 MPa	Poisson's Ratio	0.30 – 0.45
Elastic Modulus	1.5 -5 GPa	Compressive	5 -25 MPa

Table (3) Mechanical Properties of Clay

3.1 Clay / Ldpe

Polymer–clay nanocomposites are two phase materials where nanoscale inorganic particles are dispersed in an organic polymer matrix. On a nanometer level, the inorganic fillers improve the properties of the polymer. Since the nylon–clay nanocomposites with excellent mechanical properties were developed, polymer–clay interactions have been actively studied. The most commonly used clay is montmorillonite MMT is a crystalline, 2:1 layer clay mineral in which a central alumina octahedral sheet is sandwiched between two silica tetrahedral sheets. The thickness of the platelets is of the order 1 nm and the aspect ratios are high, typically 100–1500. Low density polyethylene (LDPE) is one of the most widely used polymers as electrical insulation. LDPE–MMT nanocomposites show improved tensile strength and modulus with good flammability resistance. The improved tensile strengths were observed also at 70 °C [10-12]. In addition to higher heat resistance and flame intendency, the LDPE–MMT nanocomposites show the lower impermeability to gases and vapours, what can be the effect of barrier properties. The electric properties of LDPE–MMT nanocomposites were rarely reported. Some results indicate that addition of nanoparticles enhances partial discharge and corona resistance and affects the conduction mechanism of nanocomposites [4-6].

3.2 Clay/Hdpe

High-density polyethylene (HDPE) is considered a primary material in the materials substitution chain because of availability and recyclability. The performance criterion to encourage the application of HDPE requires superior modulus and yield strength in conjunction with high-impact strength. A substantial enhancement in mechanical properties (modulus, yield strength, and toughness) of thermoplastic materials can be realized by reinforcement with inorganic minerals including talc, mica [1-3], wollastonite, glass bead, and calcium carbonate.

In recent study [51-53] of PP–clay nanocomposites, both the crystalline and crystallization temperature of polymer nanocomposite increased, this was attributed to the nucleation role of clay. In present case, the increase in crystalline can be ascribed to the nucleating effect of nanoclay, while the reason for crystallization temperature of PE–clay nanocomposite remaining unaltered may be related to the particle–matrix interaction, The interfacial interaction plays a critical role in the free energy of cluster formation and the rate of nucleation; the weak interaction lowers the rate of nucleation.

3.3 Abs/Clay

Acrylonitrile-butadiene-styrene (ABS) polymer/clay nanocomposites were produced using an intercalation/adsorption technique from polymer in solution: polymer/clay suspensions were subjected to ultrasonic processing to increase the effectiveness of mixing. Several kinds of organically modified layered silicates (OMLS) were used to understand the influence of the surfactant nature on the inter-collation exfoliation mechanism. The addition of small fractions of nanometric filler to a polymer matrix has a large potential to improve the polymer properties. The performance of polymer-clay nanocomposites strongly depends on clay-polymer interactions, which can be improved through dispersion and exfoliation of the clay. Three typologies of composites can be defined depending on the degree of filler-matrix interactions: conventional composite, intercalated nanocomposite and exfoliated nanocomposite. In a conventional composite the clay sheets remain stacked in micrometric structures called tactoids with no increase in the layer-to-layer distance (*d*-spacing) as compared to the pristine clay; in an intercalated nanocomposite polymer chains penetrate into the interlayer region and increase the *d*-spacing; a further increase in *d*-spacing gives formation to an exfoliated nanocomposite, characterized by a disordered and homogeneous dispersion of single clay sheets. The last system is the most desirable because it maximizes the interfacial region between the filler and polymer matrix, with a subsequent improvement in reinforcement effect. ABS is a widely used engineering thermoplastic owing to its desirable properties which include good mechanical behavior and chemical resistance. However, there are still only a few reports about the preparation of ABS/MMT nanocomposites [10-15].

3.4 Pi/Clay

Organic-inorganic nanocomposites usually have unique properties because of the combination of advantages of inorganic materials like rigidity, low coefficient of thermal expansion (CTE), high thermal stability and the advantages of organic polymers like flexibility, bioelectricity, process ability etc. Due to the distribution at nano-meter size, organic-inorganic composites often exhibit some special mechanical, electronic properties which extend their application to many new sectors. Among organics, PI is well-known as high performance polymer which exhibits outstanding dielectric, mechanical properties, thermal stability and low CTE. Among different types of PIs, rigid PI are widely used in microelectronics and aerospace industries because of its unique features like high modulus, low CTE and good mechanical strength, low solvent swelling and moisture uptake and spontaneous in-plane orientation. PIs possess limitations for much higher performance applications in which inorganic materials are used, because of their intrinsic nature as organic materials. Inorganic materials exhibit excellent thermal stability and high modulus. Thus, the formation of nanocomposites of PI with inorganic materials has been suggested to meet the demands of balanced properties for both organic and inorganic materials. The most commonly used clay in the preparation of polymer/clay nanocomposites is montmorillonite (MMT). The layer of MMT is 1 nm thick and about 100 nm in length. In order to disperse the hydrophilic MMT well into organic polymers, Na ions on its surface should be exchanged by organic cations through ion-exchange process to render the surface hydrophobic. This modified MMT is called organically modified montmorillonite (OMMT). Thus, there will be hydrophobic environment into the clay galleries to accommodate the hydrophobic poly (amid acid). The presence of carboxyl

groups may enhance the interaction between OMMT and poly(amid acid) through hydrogen bonding [15,16].

3.5 Epoxy/Clay

The nanocomposites produced can be classified primarily as either intercalated, where the polymer matrix has migrated between the clay layers expanding the d-spacing, or exfoliated/delaminated, where the clay layers have been separated completely by the polymer matrix. It is generally accepted that exfoliated nanocomposites have the greatest potential for property enhancements. When the clay layers are separated completely and evenly within the polymer matrix, the extent of clay/polymer interaction is maximized. This results in the greatest enhancement of properties for certain polymers. If, for a given polymer, the maximum property enhancement can be achieved by an intercalated nanocomposite then the exfoliated nanocomposite of the same polymer would not be expected to show further enhancements. The type of nanocomposites produced depends, in part, on the polarity and viscosity of the polymer matrix [10-14]. Nanocomposite materials are expected to be obtained from combining the various epoxy resins with the organoclays. Furthermore, it is expected that the structure of the nanocomposite will depend on both the curing agent used and the specific organoclay employed. The reduction in size of the inert filler to the nanometre level should result in the best potential for initiating the multiple crazing required to increase the toughness and strength of a composite. The more individual cracks that form in a polymer network, the more energy are required for it to catastrophically fracture. However, due to the very large surface area of nanofillers, strong interparticle interactions are likely to result in cluster formation or agglomeration.

3.6 Pp/Clay

Composite materials that contain nanometer scale filler have been appeared over the last 15 years to afford remarkable property enhancements relative to conventionally scaled composites. A polymer layered silicate nanocomposite where layered silicates of nano-scale dimensions are dispersed as a reinforcing phase in an engineering polymer matrix is one of the most important forms of "hybrid organic-inorganic nanocomposites". The composite with well dispersed silicate layers exhibit a significant improvement in thermal, mechanical, barrier properties with the use of minimal amount of filler. Many polymeric systems have been investigated in this field, such as polyamide 6. Polystyrene, polyethylene terephthalate [17-26], polycaprolactone, and epoxy resin. It was found that the exfoliated/intercalated dispersion of the clay layers could be achieved in certain polymers, which have polar functional groups compatible with the polar hydroxyl groups on the silicate clay layers. Polypropylene is one of the most widely used thermoplastic materials in the plastics industry. A successfully developed PP/clay nanocomposite has a great potential being applied in the diverse areas of industry such as automobile, bottle, film, and package, etc. However, because of the non-polar nature of the polypropylene, it is difficult to exfoliate silicate layers and to have homogeneous dispersion of the silicate layers in PP matrix. This is because the organophilic clays have polar hydroxyl groups and are compatible only with polymers containing polar functional groups. To resolve the incompatibility between no polar polymer and polar clay, compatibilizers such as PP-g-MA and hydroxyl groups' grafted polypropylene were used. These compatibilizers

contain polar functional groups which enhance the interface interaction between the PP matrix and the clay [24-28].

3.7 Pmma/Clay

Poly (methyl-meth-acrylate) (PMMA) is a typical transparent amorphous polymer, which is used in various field of our daily life. PMMA has several desirable properties such as good flexibility, hard and stiff, low water absorption, and outstanding outdoor weathering. However, its poor thermal stability has limited its application. To improve the heat resistance, preparation of nanocomposite is an effective way. PMMA/clay nanocomposites offer potentials for enhancing gas barrier, and increasing thermal stability. In recent years, much attention has been paid to polymer-layered silicate nanocomposites, because of its enhanced physical, mechanical, and chemical properties when compared with those of pure polymer. These unique properties of polymer/clay nanocomposites resulted from high degree of dispersion of clay in polymer matrix. There are two distinct nanostructures identified in these nanocomposites, intercalated, and exfoliated. This can be achieved when the nanoscale silicate platelets are well dispersed by delaminating the layered silicate throughout the polymer matrices which results the so called exfoliated morphology [30-34].

The exfoliated nanocomposite is more desirable than the intercalated one because of the stronger synergistic effects between polymer matrix and silicate layers. However, it is still a challenging work to obtain the complete exfoliation of clay in polymer. Clays are hydrophilic inorganic compound whereas polymer contains hydrophobic group. Therefore, clays have to be modified by organic modifier containing both hydrophilic and long chain hydrophobic group to increase not only the interlayer spacing, but also the compatibility with polymer matrices. Moreover, clay is naturally occurring, environmentally friendly, cheap and readily available in large quantities. It is evident that polymer/clay nanocomposites can increase strength and stiffness, thermal stability, gas barrier property, clarity, and decreased flammability with only a small amount of clay [20-26]

3.8 Pvc/Clay

Despite this recent proliferation of nano-clays as additives for polymers in academic research and, to a lesser extent, in industrial practice, high performing clay-reinforced nanocomposites based on PVC have remained elusive. The main challenge with these systems relates to the common ammonium-based organic treatments of the clays, which typically yield an amine during the processing of the nanocomposite, and this amine can accelerate the degradation of the PVC. In order to avoid this degradation, one must use a much less-basic amine, or some other nano-dimensional material such as a layered double hydroxide, LDH, might be used. There is a recent report [67] of a PVC-LDH composite which has much better thermal stability than does PVC, probably because the hydroxides can absorb the HCl as it is evolved. Nonetheless, the HCl is still evolved with concomitant degradation of the PVC and this has not been examined [27-29].

Efforts to obtain PVC-montmorillonite nanocomposites have employed melt blending [30], solution blending and polymerization, using either the pristine sodium clay or organically-modified clays. With melt blending, degradation of the PVC typically occurs quite rapidly, accompanied by strong discoloration. When organically-

modified layered-silicate clays are used, in general good dispersion of the clay in the polymer can be achieved, normally as intercalated systems; in contrast, when pristine alkaline clays are used, the dispersion is not as good. Where mechanical properties have been examined, they appear to be improved by the addition of a small amount of clay, but are decreased with larger amounts of the clay. A study using X-ray photoelectron spectroscopy on PVC–clay nanocomposites has found that the presence of the clay seems to retard the chain-stripping process of degradation and that enhanced there formation is observed. The recent introduction of a new nano-clay, which contains a tallow-triethanol-ammonium cation, has motivated us to revisit this material to see if there is an advantage in making PVC nanocomposites [31-36].

4- AL2O3 FILLED POLYMERS

Aluminum oxide commonly referred as alumina with the chemical formula Al₂O₃ as shows in Table (4). It is a chemical compound of aluminum and oxygen with strong ionic inter atomic bonding, giving rise to its desirable material characteristics. This can exist in several crystalline phases, which can be reverted to the most stable hexagonal alpha phase at elevated temperatures. Alpha phase alumina is the strongest and the stiffest of the oxide ceramics. Its high hardness, excellent dielectric properties and good thermal properties make it the material of choice for a wide range of applications [15-20]. It is also known for its excellent size and shape capabilities with high strength and stiffness too. Alumina is the most cost effective and widely used material in the family of engineering ceramics. The raw materials from which this high performance technical grade ceramic is made are readily available and reasonably priced, resulting in good value for the cost in fabricated alumina shapes. With an excellent combination of properties and an attractive price, it is no surprise that fine grain technical grade alumina has a very wide range of applications [32].

Table 4: Physical and Chemical Properties of Aluminum Oxide [43]

1	Odors	Odorless	8	Conditions to Avoid	Incompatibles
2	Solubility	Insoluble in water	9	Water Absorption	Nil
3	Boiling point	2980 Co	10	Crystal Structure	Cubic
4	Melting point	2000 Co	11	Average Particle Size	10 – 50 nm
5	Stability	Stable under Ordinary condition	12	Specific Surface Area	35 m ² /g – 45 m ² /g
6	Hazardous Polymerization	Will not occur	13	Color	Ivory
7	Incompatibilities	Ethylene oxide			

Table 5: Mechanical Thermal and Electrical Properties of Aluminum Oxide [45]

Mechanical	Si/ Metric	Thermal	Si/ Metric	Electrical	Si/ Metric
Density	3.89g/cm ³	Thermal Conductivity	35 W/m. K	Dielectric	16.9 Kv/mm
Porosity	0.0 %	Coeff. of thermal Exp.	8.4 10- 6/Co	Dielectric	9.8 @1MHz
Flexural Strength	379 MPa	Specific Heat	880 J/Kg.K	Dissipation Factor	0.0002@1M Hz
Elastic Modulus	375 GPa			Volume Resistivity	>1014 Ohm.cm
Shear Modulus	152 GPa				
Bulk Modulus	228 GPa				
Poisson's Ratio	0.22				
Compressive Strength	2600 MPa				
Hardness	1440 Kg/mm ²				
Fracture Toughness KIC	4 Mpa. m0.5				
Maximum Use Temperature	1750 Co				

Aluminum toxicity depends on the solubility of aluminum and the presence of biologically active forms of aluminum. Effects of aluminum in environment are highly dependent on the form of aluminum as in Table (5). The toxicity portion of this paper will review the effects of aluminum oxide use for phosphate removal on corals [45]. Aluminum oxide grit powder has a wide variety of applications ranging from high temperature electrical insulators, High voltage insulators, Thread and wire guides, Electronic substrates, ballistic armor, thermometry sensors, and widely used materials in composite industry too. With an excellent combination of properties at an attractive price, nano-aluminum oxide towards to a very wide range of engineering applications.

4.1 Epoxy/Al₂O₃ [46]

Recent research has shown that dielectric properties of epoxy-resin specimens can be improved (e.g. resistance to surface degradation) by the use of nano-sized alumina fillers. The improvement was seen to be even more marked if the nanometric fillers were pre-processed before use. The dielectric material used is epoxy resin, while nano-sized alumina (Al₂O₃) is used as filler.

4.2 Pmma/Al₂O₃

The role of gel polymer electrolytes (GPE) in the technology of modern batteries [41], super-capacitors [42] and electro-chromic devices [44–47] has grown steadily recently. For most potential applications, it is desirable that the polymer electrolyte exhibits reasonable conductivity ($10\text{--}4\text{ S cm}^{-1}$), high mechanical strength, and stability over a wide range of temperature and electrochemical window. The results achieved in poly (methyl methacrylate) (PMMA)-based gel electrolytes prepared by immobilizing an inorganic salt (LiClO_4 and NaClO_4) in an aprotic solvent (propylene carbonate) in a polymer matrix were previously reported [49–50]. However, while Olyslaegers prior research has led to significant improvement, ionic conductivity remained relatively low at ambient temperature [55]. Various methods have been applied to increase the conductivity of electrolytes. One of the approaches relies upon the addition of nanocomposite sorbents. Recently, the positive influence of inert nanoparticles on either the specific conductivity or mechanical properties of gel electrolytes has been announced [56]. In the present work report the influence of dispersed nano-sized Al_2O_3 on the ionic conductivity of PMMA-based GPEs [51-53]. More-over, the GPEs prepared directly from the monomer, thermal polymerization initiator and cross-linking agent were included for comparison. Both, liquid and PMMA-based GPEs containing dissolved Li or Na ions, were studied over a wide temperature range.

4.3 Pi/ Al_2O_3

Polyimides (PI) show outstanding thermal, mechanical, and electrical properties as well as resistance to solvent and radiation, as one of the most important super-engineering plastics [35–37].

The research on the tribological behavior of PI-based nanocomposites, however, is waiting to be broadened and deepened [32,38], although the effect of inorganic nanometer filler on the tribological properties of polymer matrix composites and the mechanisms of various fillers have been roughly recognized [32, 39]. Accordingly, the tribological properties of PI-based nanocomposites incorporating different proportions of nanometer Al_2O_3 particles are dealt with in the present work, by sliding the PI nanocomposite blocks against a plain carbon steel ring.

4.4 Pp/ Al_2O_3

Traditional polymer nanocomposites have improved mechanical properties, such as toughness, as a result of the incorporation of inorganic particulate fillers [21-22]. However, high filler loadings (up to 20 % by volume) are required for such an enhancement of performance, leading to a loss of the easy process ability of the polymers. Consequently, polymer-based nanocomposites are attracting considerable attention because of the unique properties that result from their nano-scale microstructures [23, 24]. They are much lighter in weight, more transparent, and easier to process than conventional inorganic particle reinforced polymers, in addition to displaying improved mechanical properties [25-28]. However, the homogeneous distribution of inorganic nanoparticles into the polymer matrix is required to obtain the desired polymer-based nanocomposites [29-33] because agglomeration of inorganic nanoparticles caused by immiscibility between the inorganic nanoparticles and the polymer matrix leads to a reduction, rather than an improvement, of the material's

properties. The polypropylene nanocomposites were fabricated by blending surface-modified γ -Al₂O₃ nanoparticles and crosslinking agents, followed by e-beam irradiation.

4.5 Ldpe/Al₂O₃

Among thermoplastic polymers, low-density polyethylene (LDPE) is of technological interest since it is an easily processed non-polar semi-crystalline polymer, which can be used as a representative of the polyolefin family. In addition, the production of nanocomposites based on LDPE could improve the mechanical properties to levels equivalent to those displayed by high-density polyethylene (HDPE), but with a low degree of crystallinity, which would make the modified LDPE more attractive for processes such as injection molding, due to the expected reduction in cooling time and in mould shrinkage. The various applications of LDPE range from biomedical devices to use in the packaging industry. LDPE crystalline fraction can affect its mechanical properties, since stiffness and strength normally increase with increasing polymer crystallinity. The presence of fillers or additives can interfere with the polyolefin molecules fitting into the crystal structure and the overall mechanical response may decrease. Thus, the matrix–filler interface plays a decisive role in obtaining the ultimate mechanical properties [36–40].

4.6 XLPE/AL₂O₃

During the last decade innovative hip bearings such as ceramic-on-ceramic and highly cross-linked polyethylene (XLPE)-on-ceramic or metal were introduced into clinical practice. In addition, in young patients with joint destruction and sufficient bone stock there is a trend towards cement less total hip arthroplasties where typical implants such as titanium or tantalum alloys have shown excellent osteo-conductive properties allowing bony ingrowth onto the metal surface and guarantee a solid fixation of both stem and socket [41–44]. However, early implant loosening due to wear debris, induced osteolysis is still a common cause of implant failure and an unsolved problem in total hip replacement (THR) [45–47]. The idea of developing harder polyethylenes which combine resistance against cold flow with low friction rates was technically realized by different cross-linking techniques. These cross-linked polyethylene's (XLPE) have shown excellent material properties in hip simulators (low friction, low wear debris) and were introduced into clinical application in relevant numbers at the beginning of this century [53, 54]. In hip simulators XLPE liners generated significantly lower wear rates compared to conventional UHMWPE.

Most data suggest, however, that XLPE particles are smaller in diameter (0.71 vs. 0.26 μ m) raising the question whether or not these small particles are more bioactive inducing a stronger biological response in vivo [53, 54]. In addition to advances in polyethylene, Al₂O₃ ceramic femoral heads are being used with increasing frequency as articulating partners over the past three decades. Due to their biomaterial properties such as inertness, high degree of hardness and plain surface structure which allow optimal lubrication and superb wear resistance, ceramics have shown excellent clinical results [55, 56]. Therefore it has been postulated that XLPE-ceramic bearings may lead to lower wear rates and promote longevity of hip arthroplasties [57]. In contrast to several in vitro studies, there are little data on clinical outcome and wear

debris rate after XLPE liner implantation in THR patients available so far. The purpose of this study is to quantify early abrasion of Al₂O₃- XLPE and assess clinical and radiographic outcome in a defined modular and cementless total hip system [58].

5- BATIO3 FILLED POLYMERS

Barium titanate possesses excellent dielectric, ferroelectric, and piezoelectric properties; it is considered the most important type ceramic material. For achieving good dielectric properties, a material should have a fine particle size, narrow size distribution, non-aggregation, spherical morphology, and uniform composition. The following table contents some properties of Barium Titanate. The production of spherical BaTiO₃ powders at 700 and 900°C by the spray pyrolysis of ethanol/water solutions of BaCl₂ and TiCl₄ that were suspended using two-fluid and ultrasonic atomizers, respectively in Table (6).

Table 6: Selected Properties of BaTiO₃ [60]

Modulus of Rupture MOR	Elastic Modulus (E)	Theoretical Density (ρ)	Melting Temp. T_m	Piezoelectric Constant d₃₃	Coeffe. of Thermal Expansion
82 MPa	67 GPa	6.02 g/cm ³	1618 Co	191 pc/N	0.9 ×10 ⁻⁵ /Co

5.1 Epoxy/Batio3

Among various kinds of passive components, special interest is focused on capacitors, because they are used in large numbers for various important functions, such as decoupling, by-passing, filtering, and timing. In particular, decoupling capacitors, which are used for simultaneous noise suppression, are considered as the most important application area of embedded capacitors [52]. One of the promising materials for embedded capacitors is polymer/ceramic composite, polymer filled with ceramic powders [53-55]. It utilizes high dielectric constant of ceramic powders and good process ability of polymers (low temperature process & low cost). In this study, barium titanate (BaTiO₃: BT) and strontium titanate (SrTiO₃: ST) powders and epoxy resins were selected, because these powders were commercially available and well-known high dielectric constant ceramic powders. Two most important requirements for embedded capacitor materials are high dielectric constant and low capacitance tolerance.

5.2 Hdpe/Batio3

Barium titanate ceramic (BaTiO₃, BT) is considered as the most important positive temperature coefficient (PTC) ceramic materials, which can easily span across insulating regions and further connect the existing conductive pathways. BT is incorporated into the carbon black (CB) filled HDPE polymer composites to achieve a desired conductivity and further improved PTC effect. It was found that the conductivity and PTC intensity of the specimens were remarkably improved when the

concentration of BT reaches a certain level. When compared to the CB/HDPE composites, the negative temperature coefficient effect (NTC) in the CB/(HDPE-BT) composites was also weakened to some extent. These results were explained in microstructure of the CB/(HDPE-BT) composites [56-60].

5.3 Pei/Batio3

Dispersion of ceramic phases into the organic polymers is an issue of both scientific and technological interests. The search for new materials that combine large dielectric constant and low dielectric loss has become a challenging task. In the past decade, there has been an increasing interest in the studies of ferroelectric ceramic-polymer nanocomposites due to the unique combination of promising properties and construction of multifunctional structures of each component [60-62]. These nanocomposite materials possess superior physical properties such as enhanced mechanical strength and improved electric compliance.

One of the most attractive features of such composites is that their dielectric properties could be influenced by the shape, size and connectivity of the dispersed constituents in the polymeric matrix [57-59]. Polyetherimide was chosen in this study because it belongs to the polyimide family of polymers and has been proven to possess the unique combination of mechanical properties and dielectric properties [60-62]. Aromatic polyetherimides have been a material of choice in high-performance microelectronic applications because of their high degree of ductility, inherently low thermal expansion coefficient and low dielectric constants [53, 54]. However, in contrast to other conventional polyimides, PEI exhibits relatively poor solvent resistance, dimensional stability and thermal stability, which limit its extensive applications in various fields. Therefore, it is expected that the dispersion of ferroelectric ceramic nanoparticles into the PEI matrix could make high-performance nanocomposite for microelectronic applications.

Barium titanate (BaTiO_3) is one of the most used ferroelectric ceramic because of its high dielectric constant as well as unique piezoelectric and pyro-electric properties [55-57]. A good dispersion of the ceramic particles into polymer matrix implies better and homogeneous packing, resulting in uniformity of the properties and higher dielectric constant [58, 59]. It is usually difficult to attain homogeneous distribution of ceramic particles throughout the polymer matrices by conventional melt-blending process whereas in this regard, in situ polymerization could play an important role for achieving the uniform dispersion of the particles in the composites. Many reports are available on the structural, thermal and mechanical properties of PEI-based composite materials [55-62]. Most of these published experiments have utilized the conventional blending method for producing PEI-based composites, which has no real control on distribution and orientation of the dispersed particles. No systematic study to date has been published on the influence of effective volume fraction of dielectric components, applied excitation frequency and temperature on the dielectric and piezoelectric properties of the polyetherimide/ BaTiO_3 nanocomposites. In the present study, the dielectric properties of the PEI/ BaTiO_3 nanocomposite films were measured as a function of frequency, temperature and ceramic volume fraction [67-70].

6- SiO_2 FILLED POLYMERS

Fumed Silica is a fluffy white powder with an extremely low density, marketed under trade names such as Aerosil and Cab-o-sil. With both hydrophobic and hydrophilic grades available, it is widely used as a rheology modifier, imparting highly thixotropic properties at relatively low percentages. It can also provide increased track, better stability in suspensions and prevents “sagging” and settling of solids in a liquid system. For this reason it is particularly suitable for coatings, inks, adhesives, resins, sealants, and greases. Fumed silica, or fumed silicon dioxide, is produced by the vapor-phase hydrolysis of silicon tetrachloride in an H₂/O₂ flame. Hydrophilic fumed silica bearing hydroxyl groups on its surface is produced by this process. Hydrophobic fumed silica is made by processing fumed hydrophilic silica through in-line hydrophobic treatments, such as with silanes, siloxanes, silazanes, etc. Fumed silica is not listed as a carcinogen by OSHA. It can easily become airborne, making it an inhalation risk, capable of causing irritation. Amorphous fumed silica is safe to handle, thus eliminating the serious health problems associated with crystalline silica dust. It is important to differentiate between amorphous and crystalline forms of silica when evaluating its effects upon exposure. In general, fumed or pyrogenic silica, which is X-ray amorphous, is non-toxic, does not cause silicosis, and is safe to work with. However, excessive inhalation should be avoided by proper ventilation or the wearing of protective masks [62]. According to MSDS for hydrophilic fumed silica, no acute toxic effects are expected upon eye or skin contact or by inhalation [49]. Fumed silica powders used in paints and coatings, silicone rubber and silicone sealants, adhesives, cable compounds and gels, printing inks and toner, and plant protection

6.1 Pp/Sio2

Polypropylene (PP) is a versatile polymer widely used in textiles and packaging. In practice, commercial PP products available in composite forms usually contain micron-sized fillers which function as property enhancer. Recently, polymer nanocomposites have received great interest due to their superior properties when compared with conventional composite materials. Improvements in mechanical properties, such as stiffness and toughness, dimensional and thermal properties could be achieved with nanofillers. The dispersion degree of the filler greatly influences the enhancement efficiency [67, 68]. Therefore, in order to meet those excellent properties, it is very important that the average size of fillers must be present in the nanometer-sized ranges with fine particle distribution in the polymer matrix. Carbon nanotube (CNT) and montmorillonite (MMNT) have taken a lead as the nano-filler for plastics as well as fibers (34-35). Another interesting choice is nano-sized silica which has been explored as the filler for polymeric materials and held a great potential for developing high performance polymer. PP/hydrophobic silica nanocomposite films were prepared [68-70]. Two mixing methods, extrusion mixing and dissolution mixing were adopted. The obtained nanocomposites were compressed into flat film.

6.2 Epoxy/Sio2

EPOXY resins are highly crosslinked amorphous polymers used for the insulation of power transformers, switchgear, rotating machines, etc. The sensitivity of epoxy composites to humidity is a serious matter of concern because absorption of water may cause significant and possibly irreversible changes to the material [46-47].

Epoxy resins can absorb up to a few weight percent of water in a humid environment, leading to an overall degradation of the dielectric properties. Such a situation might be further exacerbated by inorganic fillers, which are often used to improve their mechanical and thermal properties and to reduce their cost. The synthesis of nanometer-sized particles is becoming routine. Because their length scale is comparable to that of polymer molecules and the high specific area of the particle surfaces within a composite, nanoparticles exhibit novel properties as fillers. Recently, research incorporating various nanoparticles into existing dielectric systems in a cost effective manner has resulted in nanocomposites with improved benefits over conventional filler systems [47-49]. However, the effect of water on nanocomposites is still far from being well established. Since the epoxy – particle interface is a potential location for water [50], nanocomposites with very high specific areas may be particularly vulnerable to the effects of such water. It is possible that a weakness caused by water will have a detrimental effect on the otherwise improved mechanical [55] and electrical behaviors experienced by incorporating nano-fillers [51-54].

6.3 Pvc/Sio2

Polyvinyl chloride (PVC) materials are extensively used in many applications, such as pipes, electric cables and sectional bars, etc. Within recent years, great attentions have been paid to modify and toughen PVC. Rubber is widely used to toughen PVC composites. However, it often leads to reduction in strength, heat resistance, modulus and difficult processing of the polymeric composites [56]. Rigid inorganic nanoparticles, for instance, calcium carbonate, silica, etc, cannot only toughen PVC materials, but also improve their tensile strength, electric properties, heat resistance and radiation resistance [57–59]. However, the interfacial interaction between the inorganic nanoparticles and PVC matrix plays a crucial role in toughening the composites. An effective way to enhance the mechanical properties of PVC-based composites is to improve effective interfacial interaction between the matrix and reinforcement. It has been proposed that the dimension of interface and strength of the interaction significantly influence the ultimate tensile properties of composites [8-11].

6.4 Pei/Sio2

A ternary hybrid of bismaleimide-polyetherimide-silica (BMI-PEI-SiO₂) was synthesized by sol-gel reaction and characterized by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Organic-inorganic nanocomposites have become an effective source of advanced materials as they usually exhibit unique properties that traditional composites and conventional materials do not have. They combine the advantages of the inorganic materials (rigidity, high thermal stability) and the organic polymers (flexibility, dielectric, ductility, and processability). Moreover, they usually also contain special properties of nanoparticles that can be developed, leading to materials with improved properties for electrical, optical, structural, electro-optical, non-linear-optical, or related applications. Attribute to excellent properties, generally, aromatic polyimides have been considered as suitable polymer matrix materials for preparing advanced hybrid composites that have potential applications in the micro-electronics and air craft industries. The use of polyetherimide

(PEI) to enhance the fracture toughness of the BMI resins has been studied in previous works and desirable results have been obtained. By the introduction of PEI, the impact and fracture toughness of BMI resin both can be greatly improved [60-62].

6.5 Pi/Sio2

Polyimide (PI) films have attracted great research interests because of their special properties, such as low dielectric constant, excellent electrical and mechanical properties, which have broad applications in microelectronics industry as buffer coatings, passive layers, interlayer dielectrics and wafer scale packages. In order to further improve the related mechanical properties, such as decreasing coefficient of thermal expansion (CTE) and improving fracture property, recent works [65-67] have been focused on how to produce nano-structure PI hybrid organic-inorganic films which can combine desirable organic and inorganic characteristics together by using different fabrication techniques. Besides their applications at room and high temperatures, PI films are also regarded as important thermal and electrical insulating materials in cryogenic engineering, such as spacecraft, superconducting magnet devices and some related electronically components. The requirements for PI films in these unique applications are extremely severe and complicated, and their related mechanical properties at low temperature are very critical. There is some research reports [71] involved in the cryogenic properties of PI films, but not much about PI/SiO₂ nanocomposite films.

6.6 Abs/Sio2

Thabet, and Mobarak [68-70] recently became interested in utilizing well-dispersed silica sol for the preparation of novel polymer/silica nanocomposites, particularly that incorporating of spherical silica particles into acrylonitrile-butadiene-styrene copolymer (ABS) and that would combine the excellent properties provided by inorganic nanoparticles with the versatility and easy processing characteristics of rubber-toughened thermoplastic. In order to reach a homogeneous dispersion of the particles in the polymer matrix, colloidal silica sol was mechanically mixed with polybutadiene-g-(acrylonitrile- styrene copolymer) (PB-g-SAN) latex, and then ABS/silica nanocomposites were prepared by blending these PB-g-SAN/silica hybrids and SAN resin. The strong interfacial bonding between the SiO₂ and the ABS might be beneficial for a homogeneous dispersion of the particles in the polymer matrix, even though a completely uniform distribution of the particles cannot be achieved during this compounding process. Since colloidal silica carries negative charges under basic conditions, electrostatic attractions are likely to give rise to between the silica surface and the cationic cyano groups of the SAN. Therefore, silica nanoparticles are expected to adsorb on PB-g-SAN beads. Also the well dispersed ABS/SiO₂ hybrids can be obtained by adsorption of silica on the surface of PB-g-SAN particles through a strong interaction of hydrogen bonding between hydroxyl groups present on the silica surface and cyanogroups of PB-g-SAN, which can prevent macroscopic phase separation in the ABS/SiO₂ hybrid system [55-60].

6.7 Pmma/Sio2

Polymeric foams have been used in many applications because of their high strength-to-weight ratio, excellent thermal and sound insulations, high energy or mass absorption, and materials savings, etc. However, with the inclusion of voids into the polymer matrix, polymer foams usually exhibit low mechanical strength and poor dimension stability. Very recently [71], microcellular foams were addressed and usually defined as foams having average cell sizes in the order of 10 μm and cell densities in the order of 109–1015 cells/cm³. Compared with unfoamed polymers, the unique structure of microcellular foams generally possesses superior properties. Nano-sized filler particles have been studied as the foaming nucleants as well. Coworkers [4-7] used organically modified layered silicates (organoclay) as nucleants to produce polypropylene (PP)/clay, biodegradable polylactide (PLA)/clay, and polycarbonate (PC)/clay nanocomposite foams using a batch foaming process and supercritical CO₂ as foaming agent. Lee and coworkers [7] investigated the plate-like and cylindrical nanoparticles such as clay, carbon nanofiber (CNF), and carbon nanotube (CNT) used as nucleants to synthesize poly(methyl methacrylate) (PMMA)/clay, polystyrene (PS)/clay, PS/CNF and PS/CNT composite foams using supercritical CO₂ as foaming agent.

On the other hand, spherical nanoparticles- like silica had also been added into the polymer matrix for controlling the foam structures. Coworker [7] has controlled foaming of polymer films through restricted surface diffusion and the addition of raw nanosilica particles or CO₂-philic surfactants. He [7] and coworkers successfully prepared PC/silica nanocomposites by melt blending. After this, they foamed the nanocomposites in an autoclave by a batch process using supercritical CO₂. However, the effect of surface-functionalized silica particles on the polymer-silica nanocomposite foams has seldom been mentioned. Therefore, the comparative studies for the effect of VMS and RS particles on the cell structure, insulation properties and thermal stability of thermoplastic PSN foams [602]. The PSN materials were prepared via in-situ bulk polymerization and the PSN foams were produced in an autoclave by a batch process using nitrogen as foaming agent. The dispersion capability of silica particles in PMMA matrix and the cell structure analysis of PSN foams were examined by TEM studies and SEM images, respectively. GPC was used to determine the molecular weights of as-prepared samples. Effect of material composition on the insulation properties and thermal stability of PSN foams were investigated by LCR meter, TPS technique, and TGA, respectively [60-66].

7- ZNO FILLED POLYMERS

7.1 Ldpe/Zno

Low density polyethylene (LDPE) was chosen as a representative polymer matrix because it is widely used for electrical insulation in the cable and wire industry owing to its high breakdown strength and resistivity. Another advantage of LDPE is that it is relatively easy to mix with inorganic fillers by simple melt mixing; good dispersion of the filler particles is readily achieved. ZnO fillers were used, since ZnO is a wide band gap semiconducting material well known for its nonlinear electrical conductivity properties and it has also been studied by many researchers [67-70]. By combining the special properties of ZnO nanoparticles with LDPE, a polymeric nanocomposite

material with controlled properties could be expected. The conductivity of ZnO is much higher than that of LDPE and is dominated by the properties of its surfaces. The conductivity of the ZnO/LDPE composite is thus expected to change with the volume fraction of ZnO, as well as its particle size and particle surface chemistry. However, the detailed relationship between the filler concentration and the permittivity of the composite is still uncertain. The behavior near the percolation threshold, p_c (the filler concentration at which the resistivity starts to change rapidly), is also of interest. Classical percolation theory predicts a steep increase in permittivity as the filler concentration increases past p_c . However, p_c and the dependence of permittivity on filler volume fraction are system and processing dependent. The percolation behavior needs to be understood carefully with consideration of the physical conditions and properties of both filler and matrix that constitute the composite [68, 69].

7.2 Pp/Zno

Polypropylene (PP) is one of the most extensively used polyolefins, and with a significant portion of its applications being under outdoor environments. Its exposure to sunlight and the related degradations are important issues that have attracted active research interest [67-71]. Severe molecular chain degradation in PP can be induced when it is irradiated within the active wavelength range of 310–350 nm, which means that photo-degradation can occur easily in PP based materials. A number of reviews and research articles [70-71] have been dedicated to the mechanisms of UV-induced degradations in PP. In the majority of studies on the photo-degradation of PP or its nanocomposites, the main focuses were on the degradation mechanisms and degradation rates, and the resulting changes in the mechanical properties were rarely addressed. It is well known that the most significant consequence of UV irradiation is the embrittlement effect to the polymer, and in particular, to their surfaces. Usually surface cracks are formed due to contraction of the surface layer, which is the main cause for the serious deterioration in mechanical properties (especially the ductility) of photo degraded products. Therefore, an understanding on the effect of UV light on the mechanical properties is necessary for a better understanding on the performance of nanocomposites. It has been reported that zinc oxide (ZnO) particle and ZnO doped ceramic particle are effective UV light screen material [71].

7.3 Epoxy/Zno

Epoxy and epoxy based composites are preferred insulating materials for several electrical applications, especially printed circuit boards, bushings, GIS spacers, generator ground-wall insulation system and cast resin transformers. Recently [67-70], epoxy based nano-dielectric systems are being increasingly investigated for their electrical properties, since the introduction of nanofillers demonstrate several advantages in their properties when compared with the similar properties obtained for epoxy systems with micrometer sized fillers [51-52]. Several dielectric properties in epoxy nanocomposites have been evaluated in the last couple of years and the permittivity and tan delta values in nanocomposites are reported to be lower than that of base epoxy and micro-composites when insulating oxides are used as the fillers [53, 54]. A similar reduction in the values of permittivity and $\tan \delta$ were also observed when layered nano-silicates were dispersed in epoxy [53]. An epoxy nanocomposite

system displays high permittivity at low frequencies and high electrical conductivities with low percolation thresholds when conducting fillers are dispersed [54]. With respect to the electrical breakdown characteristics in polymer nanocomposites, several reports are available on different polymeric systems. In another study [67, 68] on the electrical breakdown characteristics in SiO₂ filled epoxy systems, it is seen that although the insulation breakdown strengths in nanocomposites are less than that of base epoxy, they can be higher if saline coated SiO₂ nano-fillers are utilized [69]. These interesting observations in the electrical properties of epoxy nanocomposites are highly encouraging and they are mainly attributed to the unique properties of nanoparticles and the dynamics at the interfacial region [59 - 61].

It can be observed from the reported investigations mentioned in the previous paragraph that most of the studies on epoxy nanocomposites were performed at filler loadings of 1% and above [67]. Since the surfaces of nanoparticles are highly active, a significant change in the electrical properties of the epoxy nanocomposites can also occur at very low nano-filler concentrations. With this expectation, this study attempts to analyze the electrical characteristics of epoxy nanocomposites at low nano-filler concentrations ($\leq 5\%$ by weight). The fillers considered for the investigations are TiO₂, ZnO and Al₂O₃, the characteristics of which are mainly insulating in nature.

7.4 Pmma/Zno

Nano-ZnO, as one of the multifunctional inorganic nanoparticles, has drawn increasing attention in recent years due to its prominent physical and chemical properties, such as chemical stability, low dielectric constant, high luminous transmittance, high catalysis activity, effective antibacterial and bactericide, intensive ultraviolet and infrared absorption. Therefore, nano-ZnO can be potentially used as catalysts, gas sensors, semiconductors, varistors, piezoelectric devices, antibacterial and bactericide, field-emission displays and UV shielding materials. Moreover, the advance of nano-ZnO particles could improve the mechanical and optical properties of the polymer matrix. However, ZnO nanoparticles, like other nanoparticles, possess high surface energy, which may result in the agglomeration of particles when ZnO nanoparticles are dispersed in organic solvent and matrices. Thereafter, it is necessary to prepare ZnO/polymer nanocomposites to prevent the formation of agglomerated nanoparticles [67-70].

10- SUMMARY

- The fracture initiation and propagation of clay–polyethylene nanocomposite is characterized by stretching of fibrils (fibrillation) inter dispersed with micro-voids. The low toughness of the clay–reinforced polyethylene in relation to neat polyethylene is related to the crystal structure and interfacial interaction between the filler and the polymer matrix.
- ABS/clay nanocomposites were obtained using OMLS with different kinds of organic surfactants in a solution process. TGA data showed that the processing temperature influences the behavior of the clays modified with quaternary ammonium salts that might degrade and catalyze the decomposition of ABS, whereas in imidazolium based nanocomposites no catalytic decomposition is observed.

- The PI-clay nanocomposite could be classified as an exfoliated nanocomposite, because of this special structure, the PI-clay nanocomposites showed a marked improvement in mechanical and thermal properties.
- The addition of clay to an epoxy resin acts as a physical barrier, which prevents some of the potential reactions from occurring. The decrease in the number of reactions means a reduction in the cross-linking.
- The thermal stability of PMMA was increased and depended on clay loading. On the side the PMMA/clay nanocomposites retain good optical properties.
- PVC composite thermal stability, as measured by a classic HCl evolution method specific for PVC, is somewhat lowered for the nanoclay composites as compared to appropriate control formulations.
- Regardless of the degradation model, the fact that nanoclay can suppress smoke generation is of great importance for numerous PVC applications where smoke suppression is of concern. Examples of applications include, among others, wire and cable, and foamed insulation.
- The thermal and mechanical properties of the composites were markedly modified by filler addition, regardless of the alumina filler properties. In particular, a significant increase of the stiffness of the polymer in the presence of the alumina particles was found, together with an enhanced abrasion resistance.
- The presence of the alumina particles increased the thermo-oxidative stability of the composites with respect to neat LDPE.
- Dielectric constant and loss tangent of the PEI/BaTiO₃ nanocomposites increase with increasing BaTiO₃ content. The variation of temperature produced little effect on the dielectric properties of PEI/BaTiO₃ nanocomposites.
- The water uptake of nanosilica epoxy composite can be considerably reduced by ensuring that the filler particles have surfaces that are functionalized to be hydrophobic. This may also improve the composites resistance to aging.
- The mechanical properties of PI/SiO₂ nanocomposite thin films at low temperature are presented. PI/SiO₂ nanocomposite films with different silica contents are synthesized by a new sol-gel processing technique.
- A novel hybrid nanocomposites incorporating ABS with silica a nanoparticle has been successfully prepared in aqueous media using a strong acid-base interaction between hydroxyl groups of silica surfaces and cyanogroups of ABS.
- The small particle size of the ZnO nanoparticles did not affect the permittivity of the composite. Therefore, the interfaces between ZnO and LDPE do not appear to contribute to the dielectric properties.
- Results from this research study indicate that the incorporation of ZnO nanoparticles into PP matrix can impart significant improvements on the photo-degradation resistance of PP to UV-irradiation.
- Epoxy nanocomposite systems with inorganic oxide fillers display some advantageous dielectric behaviors at low nanofiller loadings. The permittivity and tan delta values in the nanocomposites are found to be lower than that of microcomposites as well as unfilled systems (for few filler loadings).
- A marginal reduction in the epoxy dc volume resistivity is also observed by incorporating a small amount of nano-filler into the base material. With respect to the ac dielectric strength, although the values in nanocomposites are lower than

those of unfilled epoxy systems, when compared to microcomposites, the type of filler seems to influence the results.

ACKNOWLEDGMENT

The present work was supported by the Science and Technology Development Fund (STDF), Egypt, Grant No: Project ID 505.

REFERENCES

- [1] Ratna. D, Manoj, N.Varley, R.Singh Raman, R. and Simon GP, "Clayreinforced epoxy nanocomposites", *Polymer International*,Vol.52, No.9, pp.1403-1407, 2003
- [2] Benfarhi, S, Decker, C, Keller, L, and Zahouily, K, "Synthesis of clay nanocomposite materials by light-induced crosslinking polymerization", *European Polymer Journal*,Vol.40, No.3, pp.493-501, 2004
- [3] Yasmin A, Abot JL, and Daniel IM, "Processing of clay/epoxy nanocomposites by shear mixing", *Scripts Materialia*,Vol.49, No.1, pp.81-86, 2003
- [4] Gua B, Jia D, and Cai C, "Effects of organo-montmorillonite dispersion on the thermal stability of epoxy layered silicate nanocomposites", *European Polymer Journal*,Vol.40, No.8, pp.1743-1748, 2004
- [5] Tolle TB and Anderson DP, "Morphology development in layered silicate thermoset nanocoposites", *Composites Science and Technology*,Vol.62, No.7-8, pp.1033-1041, 2002
- [6] Chen C, Khobaib M, and Curliss D, "Epoxy layered-silicate nanocomposites." *Progress in Organic Coatings*, Vol.47, No.3-4, pp. 376-383, 2003
- [7] Lee JY and Lee HK, "Characterisation of organo-bentonite used for polymer nanocomposites.", *Materials Chemistry and Physics*, Vol.85, No.2, pp. 410-415, 2004
- [8] Luo J and Daniell M, "Characterisation and modeling of mechanical behavior of polymer/clay nanocoposites", *Composites Science and Technology*, Vol.63, No.11, pp.1607-1616, 2003.
- [9] Gua B, Jia D, and Cai C, "Effects of organo-montmorillonite dispersion on the thermal stability of epoxy layered silicate nanocomposites", *European Polymer Journal*, Vol.40, No.8, pp. 1743-1748, 2004
- [10] Becker O, Varley RJ, and Simon GP, "Thermal stability and water uptake of high performance epoxy layered silicate nanocomposites", *European Polymer Journal*,Vol.40,No1,pp.187-195,2004
- [11] Treece, M. A. and J. P. Oberhauser, "Processing of polypropylene- clay nanocomposites: Single-screw extrusion with inline supercritical carbon dioxide feed versus twin-screw extrusion", *J. Appl. Polym. Sci*, Vol.103, pp.884-892, 2007
- [12] Xu, L., S. Reeder, M. Thopasridharan, J. Ren, D. A. Shipp and R. Krishnamoorti, "Structure and melt rheology of polystyrene- based layered silicate nanocomposites", *Nanotechnology*,Vol.16, No.7, pp.514-521, 2005

- [13] Zanetti M, Valesella S, Luda MP, Costa L. "Fire and polymers IV. Materials and concepts for hazard prevention." In: Wilkie CA, Nelson GL, editors. ACS symposium series, Vol.922, pp.75–88, 2006
- [14] M. Roy, J. K. Nelson, L. S. Schadler, C. Zou, J. C. Fothergill, "The Influence of Physical and Chemical Linkage on the Properties of Nanocomposites", Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, CEIDP, pp. 183-186, 2005.
- [15] C. Zou, J. C. Fothergill, M. Fu, J. K. Nelson, "Improving the dielectric properties of polymers by incorporating nano-particles", Proc. 10th INSUCON International Electrical Insulation Conference, Birmingham, pp. 125-130, 2006.
- [16] C. Zou, M. Fu, J. C. Fothergill and S. W. Rowe, "Influence of absorbed water on the dielectric properties and glass-transition temperature of silica-filled epoxy nanocomposites", Annual Report – Conference on Electrical Insulation and Dielectric Phenomena (IEEE CEIDP), pp.321-324, 2006.
- [17] Xie X-L, Liu Q-X, Li RK-Y, Zhou X-P, Zhang Q-X, Yu ZZ. "Processability and mechanical properties of PVC/CaCO₃ nanocomposites prepared by in situ polymerization", Polymer, Vol.45, No.19, pp.6665–73, 2004
- [18] T. Tanaka, "Dielectric Nanocomposites with Insulating Properties", IEEE Trans. Dielectr. Electr. Insul., Vol.12, No.5, pp.914-928, 2005
- [19] Y. Cao, P. C. Irwin and K. Younsi, "The Future of Nanodielectrics in the Electrical Power Industry", IEEE Trans. Dielectr. Electr. Insul., Vol.11, No.5, pp.797-807, 2004.
- [20] J. K. Nelson and Y. Hu, "The impact of nanocomposite formulations on electrical voltage endurance", IEEE Intern. Conf. on Solid Dielectr., (ICSD), 2004.
- [21] T. Imai, F. Sawa, T. Ozaki, T. Shimizu, S. Kuge, M. Kozako and T. Tanaka, "Effects of Epoxy/filler Interface on Properties of Nano or Micro composites", IEEJ Trans. on Fundamental and Materials, Vol.126, No.2, pp. 84-91, 2006.
- [22] M. Roy, J. K. Nelson, R. K. MacCrone and L. S. Schadler, "Polymer Nanocomposite Dielectrics – The Role of the Interface", IEEE Trans. Dielectr. Electr. Insul., Vol.12, No.4, pp. 629-643, 2005.
- [23] S. Singha and M. J. Thomas, "Polymer composite/nanocomposite processing and its effect on the electrical properties", IEEE Conf. Electr. Insul. Dielectr. Phenomena (CEIDP), pp. 557-560, 2006.
- [24] C. Zou, J. C. Fothergill and S. W. Rowe, "A Water Shell Model for the Dielectric Properties of Hydrated Silica-filled Epoxy Nano-composites", IEEE Intern. Conf. on Solid Dielectr., (ICSD), pp. 389-392, 2007.
- [25] B. J. Ash, L. S. Schadler and R. W. Siegel, "Glass transition behavior of Alumina/polymethylmethacrylatenanocomposites", Materials Letters Vol. 55, pp.83-87, 2002.
- [26] A. M. Mayes, "Softer at the boundary", Nature Materials, Vol.4, pp. 651-652, 2005.
- [27] J. P. Eloundou, "Dipolar relaxations in an epoxy–amine system", European Polymer J., Vol.38, pp. 431-438, 2002.
- [28] J. K. Nelson and J. C. Fothergill, "Internal Charge Behavior of Nanocomposites", Nanotechnology, Vol.15, pp. 586-595, 2004.

- [29] G. J. Papakonstantopoulos, M. Doxastakis, P. F. Nealey, J. L. Barrat and J. J. de Pablo, "Calculation of local mechanical properties of filled polymers", *Phys. Rev. E*, Vol.75, pp.1 – 13, 2007.
- [30] R. C. Picu and M. S. Ozmusul, "Structure of linear polymeric chains confined between impenetrable spherical walls", *J. Chem. Phys.*, Vol.118, No. 24, pp. 11239-11248, 2003.
- [31] P. Maity, S. Basu, V. Parameswaran and N. Gupta " Degradation of Polymer Dielectrics with Nanometric Metal-oxide Fillers due to Surface Discharges", *IEEE Trans. on Dielectr. and Electr. Insul.*, Vol.15, pp. 52- 62, 2008.
- [32] R. J. Fleming, A. Ammala, P. S. Casey and S. B. Lang, " Conductivity and Space charge in LDPE Containing Nano and Micro sized ZnO Particles", *IEEE Trans. on Dielectr. and Electr. Insul.*, Vol.15, pp. 118- 126, 2008.
- [33] Y. Murakmi, M. Nemoto, S. Okuzumi, S. Masuda, M Nagao and N. Hozumi, " DC Conduction and Electrical Breakdown of MgO/LDPE Nanocomposite", *IEEE Trans. on Dielectr. and Electr. Insul.*, Vol.15, pp. 33-39, 2008.
- [34] P. Maity, S. V. Subramanyam, V. Parameswaran, S. Basu and N. Gupta " Improvement in surface Degradation Properties of Polymer Composites due to Pre-processed Nanometric Alumina Fillers", *IEEE Trans. on Dielectr. and Electr. Insul.*, Vol.15, pp. 63-72, 2008.
- [35] H Kirkici, M Serkan and K Koppisetty, " Nano/Micro Dielectric Surface Flashover in Partial Vacuum", *IEEE Trans. on Dielectr. and Electr. Insul.*, Vol.14, pp. 790-795, 2007.
- [36] Dongling Ma, Richard W., J Hong and L. S. Schadler, " Influence of Nanoparticle surfaces on the electrical breakdown strength of nanoparticle filled low density polyethylene", *J. Mater. Res.*, Vol.19, pp. 857-863, 2004.
- [37] T. Agag, T. Koga, T. Takeichi, "Studies on the thermal and mechanical properties of polyimide–clay nanocomposites", *Polymer*, Vol.42, pp. 3399–3408, 2001.
- [38] A. Sidorenko, H.S. Ahn, D.I. Kim, H. Yang, V.V. Tsukruk, "Wear stability of polymer nanocomposite coatings with trilayer architecture", *Wear*, Vol.252, pp. 946–955, 2002.
- [39] A.P. Harsha, U.S. Tewari, "Tribo performance of polyaryletherketone composites", *Polymer Testing*, Vol.21, pp. 697–709, 2002.
- [40] Ajayan PM, Schadler LS and Braun PV, "Nanocomposite Science and Technology". Wiley-VCH, Weinheim, pp. 122–131, 2003.
- [41] Kim WY, Greidanus NV, Duncan CP, Masri BA, Garbuz DS, "Porous tantalum uncemented acetabular shells in revision total hip replacement: two to four year clinical and radiographic results", *Hip Int*, Vol.18, pp.17–22 ,2008
- [42] Siegmeth A, Duncan CP, Masri BA, Kim WY, Garbuz DS, "Modular tantalum augments for acetabular defects in revision hip arthroplasty", *Clin Orthop Relat Res*, Vol.467, pp.199–205, 2009.
- [43] Landgraerber S, von Knoch M, Loer F, Wegner A, Tsokos M, Hussmann B, Totsch M, "Extrinsic and intrinsic pathways of apoptosis in aseptic loosening after total hip replacement.", *Biomaterials* , Vol.29, pp.3444–3450, 2008
- [44] Lenz R, Mittelmeier W, Hansmann D, Brem R, Diehl P, Fritsche A, Bader R, "Response of human osteoblasts exposed to wear particles generated at the

- interface of total hip stems and bone cement.”, *J Biomed Mater Res A*, Vol.89, pp.370–378 , 2009
- [45] Germain MA, Hatton A, Williams S, Matthews JB, Stone MH, Fisher J, Ingham E, “Comparison of the cytotoxicity of clinically relevant cobalt–chromium and alumina ceramic wear particles in vitro.”, *Biomaterials*, Vol.24, pp.469–479, 2003
- [46] Purdue PE, Koulouvaris P, Nestor BJ, Sculco TP, “ The central role of wear debris in periprosthetic osteolysis”, *Hss J*, Vol.2, pp.102–113 ,2006
- [47] AVatato S, Bersaglia G, Rocchi M, Taddei P, Fagnano C, Toni A, “Wear behaviour of cross-linked polyethylene assessed in vitro under severe conditions”, *Biomaterials*, Vol.26, pp.3259–3267, 2005
- [48] Tsukamoto R, Williams PA, Shoji H, Hirakawa K, Yamamoto K, Tsukamoto M, Clarke IC, “ Wear of sequentially enhanced 9- Mrad polyethylene in 10 million cycle knee simulation study.”, *J Biomed Mater Res B Appl Biomater*, Vol.86, pp.119–124, 2008
- [49] Tateiwa T, Clarke IC, Williams PA, Garino J, Manaka M, Shishido T, Yamamoto K, Imakiire A, “Ceramic total hip arthroplasty in the United States: safety and risk issues revisited.”, *Am J Orthop*, Vol.37, pp.E26–E31, 2008
- [50] Fisher J, Jin Z, Tipper J, Stone M, Ingham E, “Tribology of alternative bearings.”, *Clin Orthop Relat Res*, Vol.453, pp.25–34, 2006.
- [51] A. Thabet, Y. A. Mubarak, and M. Abdrabo, “Dielectric Properties Response of Industrial Applications by Nanocomposite Materials”, 2nd International Conference on Energy Engineering (ICEE-2010), High Institute of Energy, South Valley Universty, Aswan, Egypt, December 27-29, 2010.
- [52] A. Thabet, Y. A. Mubarak, and M. Samir, “Complex Permittivity of Composite Systems and Comprehensive Interphase Approach”, 2nd International Conference on Energy Engineering (ICEE-2010), High Institute of Energy, South Valley Universty, Aswan, Egypt, December 27-29, 2010.
- [53] A.Thabet, Y. A. Mobarak, and A. Hassan “New Nano-Composite Materials for Enhancing Performance of Surface Plasmon Resonance Sensor”, 2nd International Conference on Energy Engineering (ICEE-2010), High Institute of Energy, South Valley Universty, Aswan, Egypt, December 27-29, 2010.
- [54] A. Thabet, Y. A. Mobarak, and M. Abdrbo, “Effective Dielectric Properties for Nano-Composite Industrial Materials”, 2nd International Conference on Energy Engineering (ICEE-2010), High Institute of Energy, South Valley Universty, Aswan, Egypt, December 27-29, 2010.
- [55] Olyslaegers C, Defoort K, Simon JP, Vandenberghe L, “ Wear in conventional and highly cross-linked polyethylene cups: a 5-year follow-up study.”, *J Arthroplasty*, Vol.23, pp.489–494, 2008 .
- [56] Miyanishi K, Hara T, Kaminomachi S, Maekawa M, Iwamoto M, Torisu T, “Short-term wear of Japanese highly cross-linked polyethylene in cementless THA.”, *Arch Orthop Trauma Surg*, Vol.128, pp.995–1000 , 2008
- [57] Glyn-Jones S, McLardy-Smith P, Gill HS, Murray DW, “The creep and wear of highly cross-linked polyethylene: a three-year randomised, controlled trial using radiostereometric analysis”, *J Bone Joint Surg Br*, Vol.90, pp.556–561, 2008
- [58] Bitsch RG, Loidolt T, Heisel C, Ball S, Schmalzried TP, “Reduction of osteolysis with use of Marathon cross-linked polyethylene. A concise follow-up,

- at a minimum of five years, of a previous report.”, *J Bone Joint Surg Am* , Vol.90, pp.1487–1491, 2008
- [59] Jacobs CA, Christensen CP, Greenwald AS, McKellop H, “Clinical performance of highly cross-linked polyethylenes in total hip arthroplasty”, *J Bone Joint Surg Am*, Vol.89, pp.2779–2786, 2007
- [60] Krushell RJ, Fingerroth RJ, Cushing MC, “Early femoral head penetration of a highly cross-linked polyethylene liner vs a conventional polyethylene liner: a case-controlled study.”, *J Arthroplasty*, Vol. 20, pp.73–76 , 2005
- [61] McCalden RW, Naudie DD, Yuan X, Bourne RB, “Radiographic methods for the assessment of polyethylene wear after total hip arthroplasty.”, *J Bone Joint Surg Am*, Vol.87, pp.2323–2334, 2005
- [62] Heisel C, Silva M, dela Rosa MA, Schmalzried TP, “Shortterm in vivo wear of cross-linked polyethylene.” *J Bone Joint Surg Am*, Vol.86-A, pp.748–751,2004
- [63] Manning DW, Chiang PP, Martell JM, Galante JO, Harris WH, “In vivo comparative wear study of traditional and highly cross-linked polyethylene in total hip arthroplasty”, *J Arthroplasty*, Vol.20, pp.880–886, 2005
- [64] Hopper RH Jr, Young AM, Orishimo KF, McAuley JP, “Correlation between early and late wear rates in total hip arthroplasty with application to the performance of marathon crosslinked polyethylene liners.”, *J Arthroplasty*, Vol.18, pp.60–67, 2003
- [65] Shorez JP, Harding TS, Atkinson PJ, Walter N, “Alteration of the amount and morphology of wear particles by the addition of loading profile transitions during artificial hip wear testing”, *ProcInstMechEng [H]* , Vol.222, pp.865–875, 2008
- [66] XU H P, DANG Z M, YAO S H, et al, “Exploration of unusual electrical properties in carbon black/binary-polymer nanocomposites”, [*J*]. *Applied Physics Letters*, Vol.90, No.1, pp.152912, 2007.
- [67] O. Gouda, Y. A. Mobarak, and M. Samir, “A Simulation Model for Calculating the Dielectric properties of Nano-Composite Materials and Comprehensive Interphase Approach”, 14th International Middle East Power Systems Conference (MEPCON-2010), Cairo University, Egypt, pp. 151-156, December 19-21, 2010.
- [68] Ahmed Thabet, Youssef A. Mobarak, and S. Abozeid, ” Exponential Power Law Model for Predicting Dielectric Constant of New Nano-composite Industrial Materials”, International Conference on Materials Imperatives in the New Millennium, (MINM-2010), Cairo, Egypt, Novmber 29 – December 2, 2010.
- [69] Ahmed Thabet, Youssef A. Mobarak, and M. Samir, ”Novel Industrial Materials Enhanced Dielectric Characteristics”, International Conference on Materials Imperatives in the New Millennium, (MINM-2010), Cairo, Egypt, Novmber 29 – December 2, 2010.
- [70] A. Thabet, Y. A. Mobarak, “Dielectric Characteristics of New Nano-Composite Industrial Materials” International Conference on High Voltage Engineering and Application (ICHVE-2010), New Orleans, pp. 568-571, October 11–14, 2010.
- [71] A. Thabet, Y. A. Mubarak and M. A. Bakry, “Developing Characterization of Industrial Polymer Conducting Materials by using Nano-Metric Fillers” *Journal of Engineering Sciences (JES)*, Assiut University, Vol. 38, No. 5, pp.1227-1246, September 2010.

دراسة تحاكى تأثيرات حبيبات النانومترية على البوليمرات الصناعية وخواصها

يقدم هذا البحث التطورات الجديدة في مجال مواد البوليمرات المركبة مع حبيبات النانو. وقد اجتذبت هذه المواد الاهتمام من الأكاديميين والصناعيين على حد سواء، لأنها تظهر تحسنا هائلا في محتويات خواص البوليمرات المركبة والتعرف على أنواع وأشكال البوليمرات الصناعية، وهياكلها، وخصائص نانو مركبات البوليمرات التي تمت دراستها. فبصفة عامة، يقدم هذا البحث أيضا أمثلة تفصيلية مستمدة من الابحاث العلمية للمواد البوليمرية التقليدية التي امتلأت مركبات اصطناعية أو طبيعية غير العضوي من أجل تحسين خصائصها، أو لتقليل التكلفة كما أن هذا البحث يدرس التحقيق في العوامل المختلفة التي تؤثر على الخواص الكهربائية للبوليمرات والمواد العازلة باستخدام علوم نانو المواد. وأخيرا، فإن هذا البحث يناقش طرق كيفية تحضير ونتاج نانو البوليمرات المركبة.