

Polymer Nanocomposites as Dielectrics and Electrical Insulation—perspectives for Processing Technologies, Material Characterization and Future Applications

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ABSTRACT

Polymer nanocomposites are defined as polymers in which small amounts of nanometer size fillers are homogeneously dispersed by only several weight percentages. Addition of just a few weight percent of the nano-fillers has profound impact on the physical, chemical, mechanical and electrical properties of polymers. Such change is often favorable for engineering purpose. This nanocomposite technology has emerged from the field of engineering plastics, and potentially expanded its application to structural materials, coatings, and packaging to medical/biomedical products, and electronic and photonic devices. Recently these ‘hi-tech’ materials with excellent properties have begun to attract research people in the field of dielectrics and electrical insulation. Since new properties are brought about from the interactions of nanofillers with polymer matrices, mesoscopic properties are expected to come out, which would be interesting to both scientists and engineers. Improved characteristics are expected as dielectrics and electrical insulation. Several interesting results to indicate foreseeable future have been revealed, some of which are described on materials and processing in the paper together with basic concepts and future direction.

Index Terms — Nanocomposite, polymer nanocomposite, nanofillers, advanced materials, dielectrics, electrical insulation.

1 INTRODUCTION

THE development of nanocomposites represents a very attractive route to upgrade and diversify properties of “old” polymers without changing polymer compositions and processing. In contrast to conventional filled polymers, nanocomposites are composed of nanometer-sized fillers (“nanofillers”) which are homogeneously distributed within the polymer matrix. Due to their very high specific surface areas, a few percent nanofillers can self-

assemble to produce skeleton-like superstructures especially when anisotropic fillers with high length/diameter ratio (aspect ratio) are used. In comparison with the conventional micrometer-sized fillers, the same volume fraction of nanofillers contains billion-fold number of nanoparticles. As a result, most of the polymer of nanocomposites is located at the nanofiller /polymer interface. The conversion of bulk polymer into interfacial polymer represents the key to diversified polymer properties. As a function of the nanofiller aspect ratio it is possible to reinforce the polymer matrix and to improve the barrier resistance against gas and liquid permeation. An

important aspect of nanocomposite formation relates to processing technology. While many prefabricated nanoparticles are difficult to disperse and require special safety precaution for their handling, modern nanocomposites are formed *in situ* via shear-induced intercalation and exfoliation as illustrated by the effective diffusion of polymer in between organophilic nanoparticles.

Let us compare filled polymers with filler-added polymers. Nanofiller-added polymers or polymer nanocomposites might be differentiated from micro-filler-filled polymers in three major aspects that the nanocomposites contain small amounts, are in the range of nanometers in size and have tremendously large specific surface area. All these characteristics would reflect on their material properties. The first thing to attract interest arises from the difference in content. Conventional filled polymers usually contain a large amount of the fillers, e.g., more than 50 wt%. Therefore those materials are really mixtures of polymers with mineral fillers, resulting in big change or difference in material properties from polymers per se. In the case of nanofillers, the amount less than 10 wt% is enough, so that some of intrinsic polymeric properties, e.g., density, must remain almost unchanged even after they become nanocomposites. The second characteristics of interest are expected from filler size difference. Size is different by three orders of magnitude in length between the two kinds of materials, which would cause much more difference, i.e., roughly by nine orders in their number density. Therefore the distance between neighboring fillers are much smaller in nanocomposites than in conventional filled polymers. In many cases, the inter-filler distance might be in the range of nanometers, if fillers are homogeneously dispersed. The last, but not least, difference is concerned with the high specific surface area of fillers. The specific surface is represented by the inverse size, and then is three orders larger for nanocomposites than that for conventional filled polymers. Interaction of polymer matrices with fillers is expected to be much more in the former than in the latter. In contrast to many conventional fillers, some nanofillers are composed of polyelectrolyte nanoplatelets which disassemble and get dispersed during processing. This formation of nano-scaled polyelectrolyte complexes can have a major impact on the dielectric behavior.

These nanocomposite features offer new opportunities for designing a totally different world of dielectrics. In fact, the size of fillers and the inter-filler distance are in the range of nanometers, and the fillers would interact chemically and physically with polymer matrices, resulting in the emerging of intermediate or mesoscopic properties that belong neither to atomic nor macroscopic frame. Polymer nanocomposites have attracted scientists and engineers in that these materials are potentially endowed with unexpectedly excellent properties. Recent scientific discoveries and technical breakthroughs in the materials indicate their

upgrade from simple commodity plastics to 'hi-tech' materials with exceptional properties. The nanocomposites are made in the form of polymers containing a small amount of nanometer size fillers, or nanofillers. Polymer matrices interact with such nanofillers and are chemically bonded together in many cases. These can be called filler-added polymers rather than conventional filled polymers or filled resins. Debye shielding length is in the range of nanometers in metal, and so might be better watched in case that the effect of electrode in contact with nanocomposites is large.

There are several preceding areas of investigation and application. In the field of engineering plastics, material selection has been made on the basis of property diagrams such as Young's modulus [GPa] vs. density [Mg/m^3] or the yield strength [GPa] vs. density [Mg/m^3] from mechanical properties' point of view. Materials with lighter weight (density: less than $1.5 \text{ Mg}/\text{m}^3$) and more mechanical strength ($E = 5\text{--}20 \text{ MPa}$, $\sigma_y = 0.4 \text{ to } 1.1 \text{ MPa}$) are preferred. Much more expectation is naturally directed to thermal endurance or thermal stability, stability against aggressive chemicals, impermeability against gas, water and hydrocarbons, recyclability through re-processing and less leakage of small molecules such as stabilizers. In comparison to traditional composites, nanocomposites are certainly advantageous in (1) homogeneous structure, (2) no fiber rupture, (3) optical transparency, and (4) improved or unchanged processability.

In the field of food packaging industry, new materials with low permeability against oxygen, carbon dioxide, nitrogen and water vapor are expected. Often they should be biodegradable. They should be processed by injection/compression molding, film blowing and/or casting.

What can one expect from nanocomposite applications in dielectrics and electrical insulation? Top priority would be dielectric breakdown strength. Generally polymers would have intrinsic breakdown strength as high as $10 \text{ MV}/\text{cm}$ ($= 1 \text{ GV}/\text{m}$) at room temperature, but in practice their breakdown strength is much lower and is determined by internal defects. Therefore, nanofillers should have the effect to increase practical dielectric breakdown strength, irrespective of defects contained. In this regard, the resistance against partial discharge and treeing is greatly concerned. Mechanical strength and thermal conductivity would be also involved if compact insulation design is required. Permittivity and dissipation factors as dielectric properties should be as low as possible for electrical insulation, while the former is required to be as high as possible for capacitors. Flame retardancy is preferred for cable insulation used in the radiation field, while tracking resistance is of interest for outdoor insulators. For dc application, formation of space charge in insulation shall be contrasted. Recyclability is generally required to protect environments. All the performances described

above, as well as other characteristics, might be improved by means of nanocomposite technology.

Processing methods suitable for nanocomposites as well as their applications have been developed by *in situ* reactive blending, melt-mixing, thermo-kinetic (sheared) mixing, extrusion, blowing and injection. Materials tried for nanocomposites are polyolefin such as polyethylene, polypropylene and polyethyleneterephthalate, epoxy, elastomers such as silicone rubber and EPR/EPDM, polyamide, and polyimide for example.

Some of the favorable results have been obtained for dielectrics such as polyethylene, silicone, epoxy, polyamide, and polyimide. Fillers such as Al₂O₃, TiO₂, SiO₂ and layered silicate have been selected. Material combinations are epoxy- TiO₂, PE- TiO₂, EPDM- Al₂O₃, PE- SiO₂, polyimide- SiO₂, epoxy-layered silicate, and polyamide-layered silicate. Outstanding results based on pioneering works that several research groups have been tackling are described in the paper.

On the basis of the above description, the following items are reviewed in the paper: Concept of Nanocomposites, Materials of Interest, Processing Methods, Experimental Work and Results and Discussion on Electrical Properties.

1.1 CONCEPT OF NANOCOMPOSITES

It seems difficult to define a term of nanocomposites clearly. The paper deals with what are called polymer nanocomposites. They are usually considered as three-dimensional composites of polymers with inorganic nanofillers dispersed. In addition to those, two-dimensional nano-layered structures are investigated as nanometric dielectrics, too. Nano-structured organic-inorganic materials and nano-structured polymer-polymer substances that are both chemically synthesized from the be-

ginning are also an important field of investigation. The former is out of scope in the paper and the latter is briefly reviewed.

1.2 NANOMETRIC DIELECTRICS

A term of “Nanometric Dielectrics” was used in 1994 [1] as future research area of dielectrics. It was emphasized that our interest is shifted from “Debye relaxational culture” to “a nanotechnical culture”. The former is governed by determining statistically averaged properties, while the latter is largely affected by a molecular order of smallness of systems and system elements. Therefore, as shown in Table 1, it was suggested that phenomena to occur at nanometric scale should be explored to clarify fundamental properties and might open up a new field of applications. This term might have been defined as nanometer size dielectrics to investigate dielectric phenomena in nanometer scale. A term of “NanoDielectrics” was proposed in 2001 [2] to explore nanometric dielectrics and dielectrics associated with nanotechnology and to produce molecularly tailored materials. This concept seems to be associated with nanostructured ceramics and tailored nanocomposites.

Structures of nanometric dielectrics and their characteristics are listed in Table 1 based on the description made in the reference [1]. This deals with bulks and layered structures, and especially focuses on the interfacial aspect of nanometric phenomena, which are treated not only by the classical macroscopic theories but also by the quantum mechanical theories. This might represent that the phenomena we have to face in this field are mesoscopic in between macroscopic and atomic scales. It covers not only electrical insulation but also electronics, liv-

Table 1. Structure of nanometric dielectrics and their characteristics.

| Form | Phenomena | Factors | Materials or States | Area |
|--|---|---|--|----------------------------------|
| Inside Bulk | Cooperative Phenomena Self-ordering Electrically-induced Ordering | Dipoles van der Waals | Ferroelectrics Liquid crystals Liquid crystal polymers | Bioscience |
| | Interaction or Interdependence | Electric field Mechanical forces Chemical potential gradient Entropic potential gradient Piezoelectricity | Smart devices, sensors and actuators | MEMS |
| Dielectric-metal interfaces | Helmholtz layers Gouy-Chapman layers | Electric field Coulombic interactions Dipolar interactions | Electric double layers Electroactivity | Electrochemistry Insulation |
| | Inner Helmholtz layers as highly oriented form | Electric field & Chemical reaction Polar molecules | Electric double layers | Redox process |
| | Quantum mechanical Tunneling | Ultra-thin barriers | LB Films Molecular structures | Electronics Materials Science |
| Interactions In the plane of interfaces | Lateral charge transport | Molecularly ordered layers Ion-rich space-charge layers | Polymer insulator FET like devices | Insulation |
| | Self-assembly | Multi-layers | Conducting polymers backed by insulating polymers | Electronics |
| Interfacial planar dipole arrays | Molecular scale quasi-2D dipole orientation | Ferroelectricity | Nanometric devices for information processing | Electronics |
| STM and AFM embedded polymers | Tunneling and hopping currents | Dielectric properties Conduction | Inside Helmholtz layers and molecular layers | Insulation |

Note: STM and AFM stand for scanning tunneling and atomic force microscopes, respectively.

ing systems, MEMS, batteries and the like. It is interesting to note that, in connection to STM and AFM embedded-polymers, a field effect display (FED) has been developed using carbon nanotubes (CNT), which is considered a next generation display device. Here STM and AFM stand for scanning tunneling and atomic force microscopes, respectively.

1.3 COMPOSITE TO NANOCOMPOSITE MATERIALS [3]

In general, composites consist of two phases, i.e., a matrix and a disperse phase. Nanocomposites are named, when the disperse phases are in the range of 1 to several hundreds in nanometer (nm). What is called a "single nano particle" of 1 to 10 nm exhibits characteristics different from either atoms or low molecular bulk materials. Fullerenes, carbon nanotubes, dendrimers that have ever attracted people are in the range of 1 nm order, and then materials can be called nanocomposites, when they are combined.

Composites were developed as structural materials, where carbon fiber reinforced plastics developed in 1960's were a typical example. Emphasis was then placed on the improvement of mechanical strength and thermal endurance. Therefore other functional properties were set aside. However, the advent of nanotechnology has changed such a situation and has opened a completely different world of nanocomposites as functional materials, not simply as structural materials, but materials with optical, electrical, electronic, magnetic, chemical and biological functions

Generally nanocomposites are, thus, a material system of the form that nanoparticles are dispersed in continuous matrices. But functional nanocomposites might include layered structure devices such as photovoltaic cells, junction devices such as diodes and transistors, and surface modified materials such as DNA chips the surface of which are fixed with biomolecules, if they are all in nanometer scale. Layered devices consisting of organic and inorganic compounds and even mono-molecule transistors might be some of the ultimate goals as nanostructured devices.

Table 2 shows many examples of nanocomposites and material combinations in such a wide range of application fields that include structural and materials engineering, electronics and electrical engineering, optics and optoelectronics, catalysts, filtration membranes, bio-nanotechnology and yarn. This table includes not only polymer nanocomposites but also inorganic-inorganic nanocomposites for reference, and even somewhat different types of nanocomposites such as meso porous materials filled with polymer chains inside. Nanocomposites consist of a matrix polymer and a disperse filler for disperse type, and material 1 and material 2 for layered structure and copolymer types.

1.4 DISPERSE PHASE AND NANO-PARTICLES [4]

Nano-particles dispersed in nanocomposites are defined to lie in either size between 1 to several 100 nm. Table 3 shows examples of disperse phase ranging from sub-nm to 1000 nm. Substances in size of a few nanometers (1 to 10 nm) exhibit quite different characteristics from either atoms and molecules smaller than 0.3 nm, or bulk materials, as described above. Small-particle nanocomposites are more important as functional materials than structural materials. For example, melting point of water is markedly lowered due to the surface effect, if it is 10 nm in size inside nano-porous materials, and ice crystals formed in carbon nanotubes smaller than 1 nm in inner diameter exhibit behaviors different from bulk ice. Furthermore, quantum effects emerge in the few-nanometer region as electrical and optical properties. Quantum dots are one of the examples. Polymer membrane exhibits reverse osmosis, if its fine holes are smaller in inner diameter than 1 nm, while it shows ultra filtration, when the holes are in the range of 10 to several tens nm. Fine holes in artificial dialysis membranes are close to 1 nanometer in inner diameter, and then prevent proteins from passing through. Metal nanoparticles, fullerenes, carbon nanotubes, giant organic compounds, and mono or accumulated molecular layers are some of the examples of nanocomposites with particles having very small nanometer size.

In the range of submicrometers, the size of disperse phase become more apparent in structural materials than in functional materials, and then impact-resistant polymer nanocomposites and high-toughness ceramic nanocomposites are often optimized in filler size in this range. When the disperse phase is in the range of 10 to 100 nm, structural and optical properties are markedly affected. Rubbers and metals are reinforced by carbon black and by particles, respectively, where the smaller size would make better effect. Optical glass prefers the transparency and then limits the upper size of fillers. Titanium dioxide is optimized in its size for cosmetics so that it may pass visible light and scatter ultraviolet light. Chemical tips under development, where a series of chemical reactions such as mixing, reaction and analysis is held on a tiny tip, would require technologies in size of this range. Semiconductor tips are finely processed in the range of 50 nm by lithography.

Carbon black, which has been long used to reinforce rubbers, is generally several tens of nm. On the other hand, commercial polymer alloys include components hundred nm in size. Among them, ABS (acrylonitrile-butadiene-styrene terpolymer) resin is endowed with optimum impact resistance by controlling the size of disperse phase in the range of several hundred nm. Polymer/layered clay nanocomposites are reinforced by introducing very thin disperse phase clay layers. For example, in the case of

Table 2. Matrix and dispersion phase in nanocomposite materials.

| Area of Composites | Matrix Materials/Material 1 | Dispersion Materials/Material 2 | Remarks | |
|--------------------------------------|---------------------------------------|--|---|--|
| Structural & Materials Engineering | Rubbers | Carbon Black | Strength, Elasticity & Abrasion | |
| | Rubbers | Calcium Carbonate | | |
| | Rubbers | Silicic Acid | | |
| | Butyl Rubber & NBR | Maleic Acid Zn | | |
| | Nylon 6 | Montmorillonite | Strength & Heat Resistance | |
| | Nylon 6 | Synthetic Layered Silicate | Gas Barrier Performance | |
| | Nylon 6 | Aramid | | |
| | PET | Aromatic Polyester | | |
| | PMMA | Pd | | |
| | ABS | Butadiene | Impact Strength & Toughness | |
| | PBT | Ethylene Copolymer | | |
| | PP | EPR/Talc | | |
| | PS | Polyphenylene Ether (Miscible) | Polymer Alloy | |
| | Nylon 6 | Polyphenylene Ether (Miscible) | Nanodispersion by Miscibilizers | |
| | Conventional Plastics | Biodegradable Plastics | Polymer Alloy | |
| | Biodegradable Plastics | Clay Compounds | Intercalation | |
| | Rubbers | Thermoset Resin | Adhesives | |
| | Ni | Y ₂ O ₃ (Dispersion) | Creep & Strength | |
| | Al | Al ₂ O ₃ (Mechanical Alloy) | | |
| | Al ₂ O ₃ | Si ₃ N ₄ | Toughness & Flexural Strength | |
| | Si ₃ N ₄ | TiC | | |
| | NiCr Alloy | ZrO ₂ | Gradient Function | |
| | SiC | TiC | | |
| Polymers | Carbon Nanotubes | Reinforcement | | |
| Al | Carbon Nanotubes | | | |
| C60 | Carbon Nanotubes | | | |
| Electronics & Electrical Engineering | Rubber | Conducting Nanoparticles | Conducting Polymers | |
| | PMMA | Polypyrrole (Continuous Dispersion) | | |
| | PMMA Microparticles | Polypyrrole (Nanolayer Coated) | | |
| | Polyaniline | MoS ₂ (Layered Compound) | (+Sliding Performances) | |
| | Conventional Polymers | Polyaniline, Polythiophene, Polypyrrole | Electromagnetic Shielding, Anti-statics | |
| | Zeolite (Nano Porous Material) | Conducting Polymers | Electromagnetic Properties | |
| | Rubber | Magnetic Nanoparticles | Magnets | |
| | Polyaniline | Iron Oxides | Magnets | |
| | PTZ (Piezoelectric) | Al ₂ O ₃ , ZrO ₂ | Mechanical Strength | |
| | PTZ (Piezoelectric) | PbO, Pt | Piezoelectricity | |
| | ZnO (Varistor) | Bi ₂ O ₃ , CoO, MnO ₂ , Sb ₂ O ₃ , Cr ₂ O ₃ | Varistor Performance | |
| | HTS Ceramics | Protective Metals (Sol-Gel Method) | Superconducting Wires | |
| | Poly(3-Alkylthiophene) | Fulerene C60 | Photovoltaic Cells | |
| | Polyphenylenevinylene | Fulerene C60, Carbon Nanotube | Photovoltaic Cells | |
| | Conducting Polymers | Photochromic Liquid Crystals | Photochromic Devices | |
| | Paste Plastics | Carbon Nanotubes (Dispersed) | Field Emitters for Image Display | |
| | SiO ₂ | Carbon Nanotubes (Junction) | Field Effect Transistors | |
| | Metallic Carbon Nanotubes | Semiconducting Carbon Nanotubes | Junction Devices | |
| | HTS Ceramics | HTS Ceramics | Josephson Devices | |
| | LB Films | Al | MIM Devices | |
| | Phthalocyanine LB Films | Aliphatic Acid Cd Salt | MS Devices | |
| | Micro Arrays | Single Chain DNA (Immobilized) | DNA Chips | |
| | Micro Arrays | Antibody Protein (Immobilized) | Protein Chips | |
| Meso Porous Materials | Organic Silylation | Resist | | |
| Optics & Optoelectronics | Inorganic Glass | Cu Phthalocyanine | Optical Absorption/Coloration | |
| | Inorganic Glass | Rhodamine, Coumarine | Fluorescence | |
| | Metals | Metal Oxides | Selective Reflection & Absorption | |
| | Polymers | Organic Compounds | Solar Cells & EL Devices | |
| | Meso Porous Materials | Azo Benzene (Connoted) | Optical Switches | |
| | Inorganic Glass | Sm | Hole Burning | |
| | Inorganic Glass | 1,4 Dihydroxy Anthraquinone | | |
| | Inorganic Glass | AgCl | Photochromics | |
| | Inorganic Glass | Spiropyran | | |
| | Inorganic Glass | Nd+3 | Laser | |
| | Inorganic Glass | Peryl-imide, Coumarine | | |
| | Meso Porous Materials | Pyridine (Connoted) | (Micro Single Crystal) | |
| | PMMA, Polycarbonate | Organic Nanoparticles | Nonlinear Optics | |
| | Inorganic Glass | CdS, CdSe, CuCl, Au | | |
| | Inorganic Glass | Organic Compounds | | |
| | Meso Porous Materials | p-Nitroaniline | | |
| | Mesoporous Silica | Polyethylene | | |
| | Mesoporous Silica | Polydiacetylene | | |
| | Gelatine | AgBr (Photosensitizers Dispersed) | Image Record | |
| | Binder | Organic Nanopigments | (Electro Photo) | |
| | Catalysts | Noble Metals | Silica & Alumina (Immobilized) | |
| | | Polymer Surfactants | Noble Metal Nanoparticles (Colloid) | |
| | | Hectorite (Layered Compound) | Alumina (Crosslinked) | |
| Ceramics, Polymers etc. | | Enzyme (Immobilized) | | |
| Meso Porous Materials | | Porphyrin Metal Complex (Immobilized) | | |
| Meso Porous Materials | | Metals & Semiconductors (Immobilized) | | |
| Filtration Membranes | Carbonate | Dimethylsiloxane (Block Copolymer) | Gas Filters | |
| | PAN | PEO | Artificial Dialysis | |
| | Polysulfone | Polyvinylpyrrolidone | Artificial Dialysis | |
| | Dimethylsiloxane | Imide (Block Copolymer) | Organic Liquids/Vapor Separation | |
| | Poly-4 Fluoroethylene Matrix | Sulfonic Acid Radical Nanoclusters | Polymer Electrolytes: Nafion Membrane | |
| | PET Films with Nanoholes | Polymer Electrolytes | Fuel Cells, Batteries | |
| Bionanotechnology | Polyetherpolyurethane | Micro Phase Separation Structures | Anti blood-clot | |
| | Polymers | Hepann (Surface Modified) | Anti blood-clot | |
| | Superfine fibers | Polymyxin (Immobilized) | Septicemia Treatment | |
| | Polymer Chams | Medicine (Immobilized) | Drug Delivery Systems | |
| | Metals, Semiconductors, Polymers etc. | Enzyme (Immobilized) | Biosensor | |
| | Biomaterials | Monoclonal Antibodies (Immobilized) | Test Medicine | |
| | Biomaterials | DNA | DNA Probes | |
| | Hydrophilic Polymers | Biodegradable Polymers | Alloy: Tissue Cultivation Scaffold | |
| | Yarn | Poly(p-phenyleneterephthalamide) | Jet Spinning | |

Table 3. Sizes of dispersion phase in nanocomposites.

| | 0.1 nm | 1 nm | 10 nm | 100 nm | 1 μ m |
|---|--------|-------|-------|--------|-----------|
| Structural Materials | | | | | |
| Natural Rubber/Carbon Black | | | ----- | | |
| ABS Resin | | | | ----- | |
| PA/All Aromatic Polyamide Alloy | | | ----- | | |
| Nylon/Clay Interlayer Intercalation | | ----- | | | |
| Nanocomposite Metals | | | ----- | | |
| Nanocomposite Ceramics | | | | ----- | |
| Functional Materials | | | | | |
| Silver Salt Photo | | | | | ----- |
| Polymer Alloys (Blend) | | | | ----- | |
| Block Copolymers (Bulk, Semi-transparent) | | ----- | | | |
| Surface Graft | | ----- | | | |
| Biomaterials & Physiologically Active Substances (Surface Immobilization) | ----- | | | | |
| Optofunctional Glass (Sol-Gel Method) | | | ----- | | |
| Films | | | | | |
| Spin Coat Method | | | | ----- | |
| Vacuum Evaporation | | | ----- | | |
| Mono or multi molecular layers | | ----- | | | |
| Nanoparticles | | | | | |
| Metal Nanoparticles | | ----- | | | |
| Fullerene | ----- | | | | |
| Carbon Nanotube | | ----- | | | |
| Dendrimer | | ----- | | | |

nylon/montmorillonite nanocomposite, montmorillonite layers become separated by 1 to 2 nm being exfoliated into nylon matrix. Disperse phase of several tens of nm is obtained for aliphatic polyamide/all aromatic polyamide alloy by the solution blend method, resulting in significant mechanical reinforcement. However, this method is very expensive, and then the melt compound method is being explored for production on a commercial base. The melt compound method utilized for PET/all aromatic polyester alloys gives inadequate reinforcement, since disperse phase is limited to around 1 μ m in size due to processing difficulty. Methods for dispersion should be improved in this case, including development of compatibilizers.

A functional material that has been used for a long time is silver salt for photo films. Size of silver bromide as a photosensitizer is usually larger than 1 μ m, and is required to be several tens to hundreds in nm for more fine pictures. Nano-particles dispersed by the sol-gel method for functional optical glass are several tens of nm in size. Blended polymer alloys are often used as functional materials. In this case, the size of disperse phase is similar to that for structural nanocomposites. Block copolymers used for bulk materials and transparent materials are provided with micro phase separation structures of several nanometers. In case of surface modification by graft, a surface layer is thinner than that. Surface layers of enzymes sur-

face-immobilized to biomaterials and physiologically active substances, DNA probes, DNA chips, protein chips, and columns immobilized to polymyxins for septicemia treatment are as thin as below 1 nm. Nano thick films are often formed by the vacuum evaporation method and the spin coating method, and they are in the range of several tens to hundreds of nm. Monomolecular and accumulated molecular layers typical for LB films are often thinner than 1 nm. Functional particles such as noble metal nanoparticles, carbon nanotubes, fullerenes and dendrimers are in the order of 1 nm.

2 MATERIALS OF INTEREST

2.1 POLYMER NANOCOMPOSITES [3, 4]

Polymer nanocomposites are understood as polymers in which nanofillers are homogeneously dispersed, but also layered structures in nanometric scale shall be included in this category. In disperse type, nanofillers are usually organically modified to be miscible with companion polymers. Polymer/layered silicate or clay nanocomposites are most popular now as polymer nanocomposites, in which silicate or clay is micaceous in shape. They could be dated back to 1990, when they were industrially manufactured as structural materials or engineering plastics for the first time. This success initiated further significant research ac-

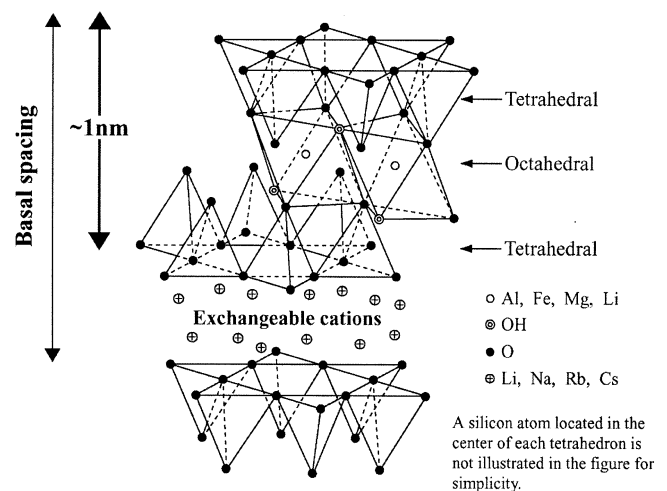
Table 4. Polymers for layered silicate nanocomposites.

| | |
|------------------------------|---|
| Vinyl Polymers | Vinyl addition polymers derived from common monomers such as methyl methacrylate, methyl methacrylate copolymers, other acrylates, acrylic acid, acrylonitrile, styrene, 4-vinylpyridine, acrylamide, poly(N-isopropylacrylamide), tetra-fluoro ethylene Selective polymers such as PVA, poly(N-vinyl pyrrolidone), poly (vinyl pyridine), poly(ethylene glycol) poly (ethylene vinyl alcohol), poly (vinylidene fluoride), poly (p-phenylenevinylene), polybenzoxazole, poly (style-co-acrylonitrile) ethyl vinyl alcohol copolymer, polystyrene-polyisoprene diblock copolymer |
| Condensation (step) Polymers | Nylon 6, several other polyamides, poly (ϵ -caprolactone)(PCL), poly (ethylene terephthalate), poly (trimethylene terephthalate), poly (butylene terephthalate), polycarbonate (PC), PEO, ethylene oxide copolymers, poly (ethylene imine), poly (dimethyl siloxane), polybutadiene, butadiene copolymers, epoxidized natural rubber, epoxy polymer resins, polyurethanes, polyurethane urea, polyimides poly (amic acid), polysulfone, polyetherimide, fluoroopoly (ether-imide) |
| Polyolefins | polypropylene (PP), polyethylene (PE), polyethylene orionomers, copolymers such as poly (ethylene-co-vinyl acetate) (EVA), ethylene propylene diene methylene linkage rubber (EPDM), poly (1-butane) |
| Specialty Polymers | the N-heterocyclic polymers such as polypyrrole (PPY), poly (N-vinylcarbazole) (PNVC), polyaromatics like polyaniline (PANI), poly)p-phenylene vinylene), related polymers liquid crystal polymer (LCP)-based nanocomposites, hyper-banded polymers, cyanate ester, Nafion, aryl-ethanyl-terminated coPoss imide origomers |
| Biodegradable Polymers | PLA, poly (butylene succinate) (PBS), polyhydroxy butyrate, aliphatic polyester |

tivities on a variety of nanocomposites for other purposes, too, e.g. nanoparticles such as TiO_2 , SiO_2 and Al_2O_3 can be mixed into polymers to form nanocomposites.

2.1.1 POLYMER/LAYERED SILICATE NANOCOMPOSITES [5]

Various polymers are feasible as layered silicate nanocomposites, which include vinyl polymers, condensation (step) polymers, polyolefins, specialty polymers, and biodegradable polymers, as shown in Table 4. Layered silicates belong to the family of 2:1 phyllosilicates, as shown in Figure 1 [4]. Their crystal structure consists of layers made up of two tetrahedrally coordinated silicon atoms fused to an edge-shared octahedral sheet of either aluminum or magnesium hydroxide. The layer thickness is around 1 nm, and the lateral dimensions of these layers may vary from 3 nm to several – micrometers or larger, which depend on the particular layered silicate. Stacking of the layers leads to a regular van der Waals gap between the layers called the interlayer or gallery. Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+} , or Mg^{2+} replaced by Li^{1+} generates negative charges that are counterbalanced by alkali and alka-

**Figure 1.** Structure of 2:1 phyllosilicates. Drawn based on [5].

line earth cations situated inside the galleries. This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC). This charge is not locally constant, but varies from layer to layer, and should be considered as an average value over

the whole crystal. Montmorillonite, hectorite and saponite are the most commonly used layered silicates.

There are two types of structure: tetrahedral-substituted and octahedral substituted. In case of tetrahedrally substituted layered silicates, the negative charge is located on the surface of silicate layers, and hence, the polymer matrices can react more readily with these than with octahedrally-substituted material. Two distinct but interrelated features characterizes layered silicates. The first is the ability of the silicate particles to disperse into individual layers. The second is the ability to finely tune their surface chemistry through ion exchange reactions with organic and inorganic cation. Pristine layered silicates usually contain hydrated Na^+ or K^+ ions. These are only miscible with hydrophilic polymers such as poly (ethylene oxide) (PEO), or poly (vinyl alcohol) (PVA). To make these miscible with other polymers, their surface should be converted to an organophilic one, which can be realized by ion-exchange reactions with cationic surfactants such as alkylammonium and alkylphosphonium cations.

Three different types of polymer/layered silicate nanocomposites are thermodynamically achievable, namely intercalated, flocculated and exfoliated nanocomposites, as illustrated in nanometric scale in Figure 2 [5]. In intercalated nanocomposites, the insertion of a polymer matrix into the layered silicate structure occurs in a crystallographically regular fashion, regardless of the clay to polymer ratio. Intercalated nanocomposites are normally interlayer by a few molecular layers of polymer. Properties of the composites typically resemble those of ceramic materials. Flocculated nanocomposites are conceptually the same as intercalated ones. However, silicate layers are sometimes flocculated due to hydroxylated edge-edge interaction of the silicate layers. In exfoliated nanocomposites, the individual clay layers are separated in a continuous polymer matrix by an average distance that depends on clay loading. Usually, the clay content of exfoliated nanocomposites is much lower than that of intercalated nanocomposites.

2.1.2 POLYMER/METAL OXIDE NANOCOMPOSITES

In a composite, the polymer in the vicinity of the filler is strongly affected by the presence of the filler and the area surrounding the filler particle is called the interphase or the interaction zone, as shown in Figure 3 [6]. For nanocomposites, the volume fraction of the polymer adjoining the filler is large due to the large surface area. It is well known that the polymer chains interacting with the surface of the filler have altered properties such as crystallinity, crosslink density, mobility or conformation. Therefore, the interface chemistry and interfacial strength is a much more critical parameter in nanocomposites than in traditional composites. Further, since these interaction zones overlap at relatively low volume fractions, it has been

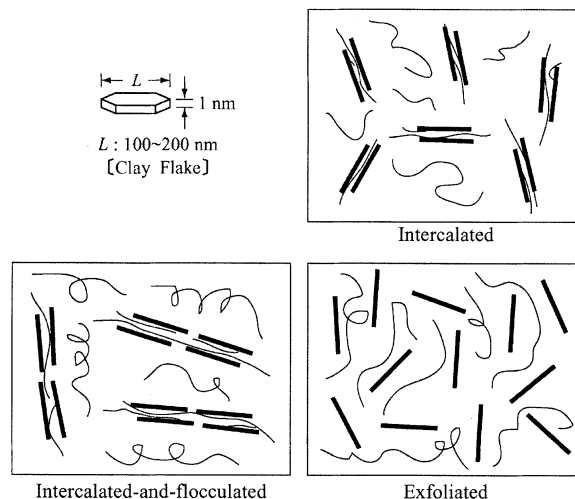


Figure 2. Schematic illustration of three different types of polymer/layered silicate nanocomposites. Drawn based on [5].

proposed that a small amount of nanofillers can have a profound affect on material properties. But unfortunately, such interaction zones are not necessarily well characterized. It was also suggested that free volume in such interaction zones would be affected by nano-fillers [7, 8].

2.2 DIELECTRICS AND ELECTRICAL INSULATING MATERIALS

Polymer matrices with dispersed inorganic nanoparticles are now a target for investigation in the dielectric field. Performance improvement as dielectrics and electrical insulation is expected. Both thermoplastic resins and thermoset resins are being considered and their companion nanoparticles are selected from clay (layered silicates), silica (SiO_2), rutile (TiO_2), and alumina (Al_2O_3). Disperse phases, nanoparticles or nanolayers of interest vary in size as indicated in Table 3. Layered silicates or clays are in the range of a few nm in thickness, and in the range of 100 nm in other two dimensions. Size of nanoparticles of inorganic substances such as SiO_2 , TiO_2 and Al_2O_3 are chosen to be 30 to 40 nm. Polymer materials such as PE, PP, EVA, EPDM, PA, PI and epoxy are under investigation.

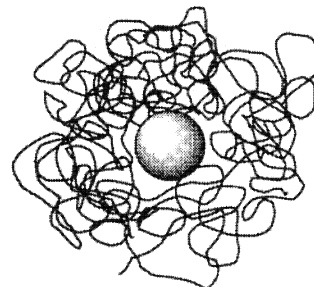


Figure 3. Illustrated morphology of polymers around metal oxides [10].

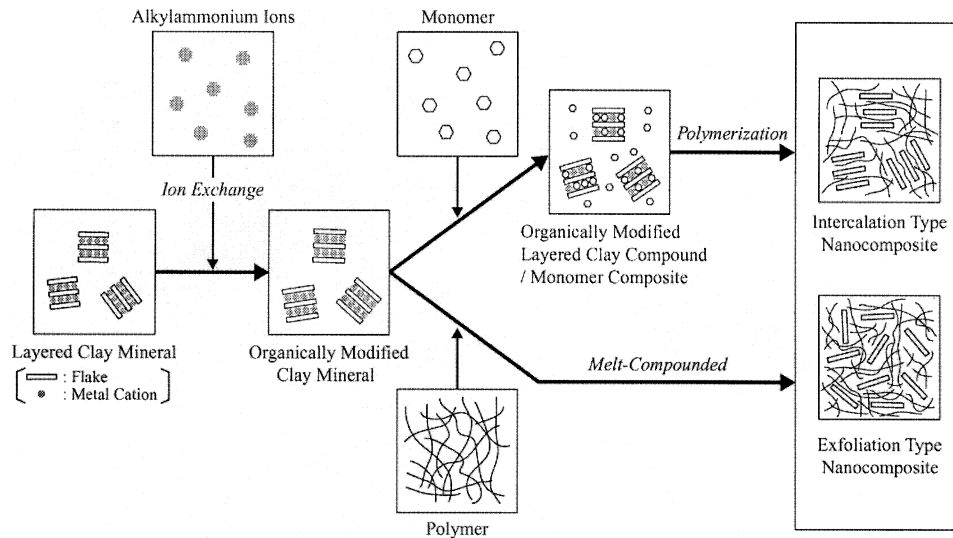


Figure 4. Intercalation and exfoliation process for polymer nanocomposites [19].

3 PROCESSING METHODS UNDER DEVELOPMENT

Composite materials consist of at least two different kinds of material phases, and therefore inherently have the interfaces with which they both contact each other. In order to form a stable composite system, it is requisite to increase the compatibility between them, and decrease the interfacial tension between them to the utmost. Especially nanocomposite materials include nanoparticles that are dispersed in nanometer scale separation even with their small addition as shown in Table 3, and are enormously large in their total surface areas. Thus it is technically required to form such a material system stably without agglomeration and phase separation for production of nanocomposites. There are several methods for nanocomposites such as intercalation, sol-gel, molecular composite and direct dispersion, as shown in Table 5. Interfacial states between both of the two phases are modified in certain ways so as to form their stable systems. In general, the interfacial tension is required to be below 10^{-4} N/m for polymer alloys of micrometer phase separation type, and below 5×10^{-4} N/m for polymer composites with micrometer-sized fillers. In case of nanocomposites, these values should be far less than those.

Table 5. Preparative methods for polymer nanocomposites.

| |
|--|
| (1) Intercalation Method |
| (a) Polymer or Pre-polymer Intercalation from Solution |
| (b) In-situ Intercalative Polymerization |
| (c) Melt Intercalation |
| (2) Sol-Gel Method |
| (3) Molecular Composite Formation Method |
| (a) Liquid Crystal Polymer Alloy Formation Method |
| (4) Nanofiller Direct Dispersion Method |
| (5) Other Methods |

The layer exfoliation and intercalation method is one of the present major methods for polymer nanocomposites. There are two processes available at present to conduct it, i.e., the polymerization process, and the melt compound process. The former was first available in public in 1987 and has been favored since then. The latter, however, seems to have been a main stream for this type of nanocomposites, since it costs less in equipment and renders the flexibility in application. The sol-gel method now attracts much more attention, because it might be comparatively easily modified to suit to industrial manufacture. Molecular composites are to be manufactured by the solution re-precipitation method, and by the melt compound method. The latter is a new method in this manufacturing process that is expected to emerge. It is necessary to develop nanometric liquid crystal polyester (LCP) fibrils to realize an industrial manufacture line for the molecular composites.

3.1 INTERCALATION METHOD

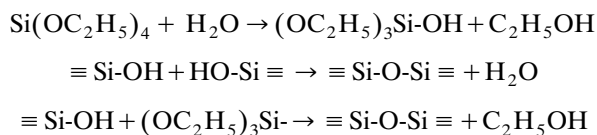
The intercalation method is the most popular for polymer nanocomposite formation. This is the method to intercalate monomers or polymers between layers of inorganic layered substances to cause to disperse them into polymers during a process of polymerization or melt compounding by exfoliating the layered substances each by each layer. Layered silicates are often used in this method, as shown in Figure 4.

There are three methods in this category [5]. The first one, i.e., intercalation of polymer or pre-polymer from solution is based on a solvent system in which the polymer or pre-polymer is soluble and silicate layers are swellable. The layered silicate is first swollen in a solvent, such as water, chloroform, or toluene. When the polymer and layered silicate solutions are mixed, the polymer chains in-

tercalate and displace the solvent within the interlayer of the silicate. Upon solvent removal, the intercalated structure remains, resulting in polymer/layered silicate nanocomposite. In the second one, i.e., *in-situ* intercalative polymerization method, the layered silicate is swollen within the liquid monomer or a monomer solution so that the polymer formation may occur between the intercalated sheets. Polymerization is initiated either by heat or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step. The last one, i.e., melt intercalation method involves annealing, statically or under shear, a mixture of the polymer and organically modified layered silicate above the softening point of the polymer. This method has great advantages over either *in-situ* intercalative polymerization or polymer solution intercalation. Firstly, it is environmentally benign due to the absence of organic solvents. Secondly, it is compatible with current industrial process, such as extrusion and injection molding. The melt intercalation method allows the use of polymers that were previously not suitable for the other two methods.

3.2 SOL GEL METHOD

The sol gel method is characterized by the fact that inorganic or composite organic-inorganic materials are made at relatively low temperatures, and in principle, consists of hydrolysis of the constituent molecular precursors and subsequent polycondensation to glass-like form. It allows incorporation of organic and inorganic additives during the process of formation of the glassy network at room temperature. This method has been traditionally utilized to fabricate glasses and ceramics. Recently, at the same time, it has been used for polycrystals, porous composites, and organic-inorganic composites. Sol-gel reaction is started from metal alkoxide, $M(OR)_n$. It should be melted in water, alcohol, acid, ammonia, and the like in order to be homogeneously dispersed. Metal alkoxide is hydrolyzed through reaction with water and turns out to be metal hydroxide and alcohol. There are many kinds of metals utilized such as Na, Ba, Cu, Al, Si, Ti, Zr, Ge, V, W and Y. Silicon alkoxides such as tetraethoxysilane (TEOS) and tetramethoxysilane (MTEOS) are often used. In case of TEOS, for example, an amorphous polymer with three dimensional network structures of silica is formed by polymerization reaction followed by hydrolysis [3].



The sol gel method was not considered suitable for mass production, since it used water as media in general. However, it is now expected to become a key technology in the near future, as new modified methods such as a continuous sol-gel have been developed recently. Various compa-

nies have introduced highly functional organosols of silic acid, produced either by sol/gel condensation of tetraethoxysilane, or acidification of sodium silicates, followed by functionalization with various trisalkoxysilanes. Another very versatile sol/gel route led to the industrial preparation of dispersible boehmite nanofillers. In the Sasol process aluminum or magnesium metal is activated by etching off the surface oxide layer. Reaction with alcohol produces alkoxides and hydrogen. Upon hydrolysis the aluminalkoxides from boehmite mineral that is obtained as nanoparticle dispersion. The boehmite minerals can be rendered organophilic by reaction with carboxylic or benzenesulfonic acids. The by-product alcohol is recycled in this process. In contrast to natural organophilic boehmite, the sol/gel reaction product is much easier to redisperse and does not possess other metal ions as impurities.

3.3 MOLECULAR COMPOSITE FORMATION METHOD: POSSIBILITY FOR NANOCOMPOSITES

Molecular composite is a material system wherein discrete reinforcement is achieved with molecular rods. It was characterized originally by the fact that a rigid polymer such as liquid crystal polyester (LCP) was dispersed in a flexible polymer matrix in molecular or microfibril dimension. This past method was conducted by such a way that two kinds of materials were melted in a co-solvent to be precipitated afterwards. It was not built up to mass production. A new method was developed in 1990's that engineering plastics were melt-compounded with small amounts of liquid crystal polyester (LCP). This was found to produce composites with excellent properties, and have attracted people's attention since then [9]. Typical examples of this type are polyamide, poly phenylene ether alloy, polyethyleneterephthalate, and polycarbonate with all aromatic polyester (LCP). It should be noted that they need the third substance that would function as compatibilizers. The third substance would work to promote the formation of fibrils and to disperse it in the composites. It is recognized that the molecular composites have more advantage over pristine materials in mechanical properties. In this case, microfibrils to be used are 500 nm in their size. In order to put nanocomposites of this type in reality, it is necessary to put disperse phase down to one order smaller than that we have now

3.4 NANO-PARTICLE DIRECT DISPERSION METHOD

In this method, nano-particles are chemically modified on their surfaces to increase compatibility with polymers, and are mixed with a polymer and dispersed homogeneously without agglomeration. There are several examples such as photo-hardening coating agents with modified silica nano-particles, nano-particle paste of gold or silver protected by comb-shaped block copolymers, and

polyamide 6 nanocomposite with silica nano-particles surface-treated by amino butyric acid.

4. EXPERIMENTAL WORK AND RESULTS

4.1 SURFACE CHANGE OF POLYAMIDE NANOCOMPOSITE CAUSED BY PARTIAL DISCHARGES [10]

Polyamide 6 used for experiments was manufactured by Unonica Co. in such a way that layered silicates, i.e., synthetic mica, were exfoliated to about 1 nm thick layers, and they were uniformly dispersed in a polyamide 6 resin by *in-situ* polymerization. Partial discharge (PD) degradation was investigated for polyamide 6 without nanoscale fillers (nanofillers) and polyamide 6 nanocomposites with 2, 4 and 5 wt% addition of organically, grafted *in situ* with polyamide. Such materials were subjected to partial discharge under the IEC (b) electrode configuration for evaluation. Comparisons were made as to the surface roughness observed by scanning electron microscopy and atomic force microscopy. It was found that the change in the surface roughness was far smaller in specimens with nanofillers than those without fillers, and that the 2wt% addition was sufficient for improvement, as shown in Figure 5. This result indicates that polyamide nanocomposite is more resistive to PDs than polyamide 6 without nanofillers.

From SEM image observation, it seems that partial discharges would attack the surface of nanocomposite, but degrade the part of polymer regions between nanofillers selectively, and even step aside from the fillers to intrude into their backside. It is to be noted that the nanofillers are more resistant against PDs, and larger in permittivity than the polymer *per se*.

A mechanism for PD degradation has been investigated. Figure 6 illustrates how PD possibly acts on the surface of PA/layered silicate nanocomposite for clarification of the mechanism. The nanocomposite consists of a group of nanometric spherulites formed around nanofillers. Regions between such spherulites are filled with amorphous PA. PD resistance is stronger for layered silicate than for polyamide. PA spherulite regions seem to have stronger PD resistance than PA amorphous regions. Permittivity of layered silicate is about twice larger than that of polyamide itself. A hypothetical model for explanation of PD resistance of this material is considered as follows. PD will concentrate on the nanofillers (about twice) on the surface of a nanocomposite specimen due to the difference in permittivity, but the nanofillers are more resistant against PD than the PA matrix. Spherulites might help to resist against PD, either. PD might be faint on the amorphous regions that are less resistant against PD. This explanation supports the experimental fact that PA/layered silicate nanocomposite is more resistant against PD than pure PA. How PDs degrade the

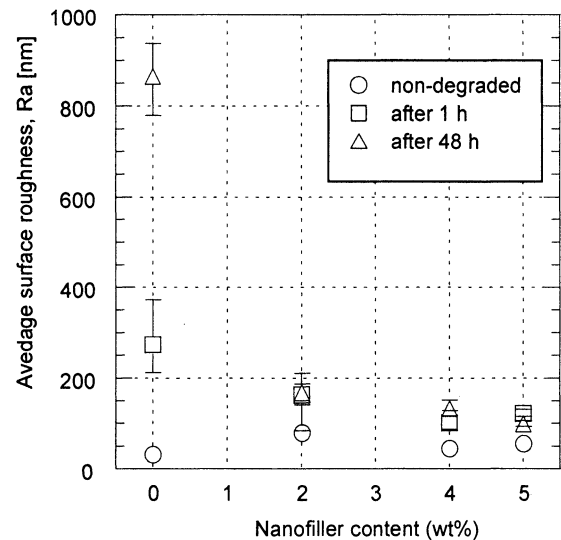


Figure 5. Relation between average surface roughness and nanofiller content. $V = 6$ kV, $t = 1$ and 48 h [8].

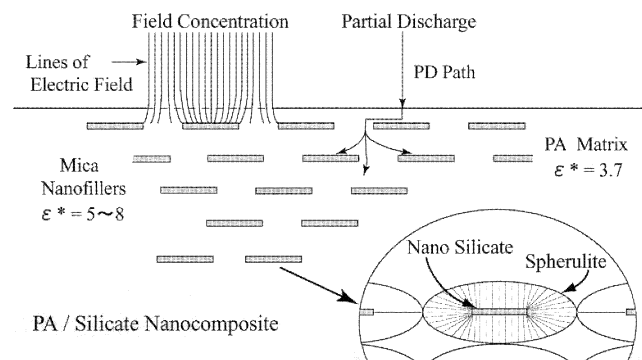


Figure 6. Schematic illustration of possible mechanisms for PD resistance of polyamide/layered silicate nanocomposite (hypothesis).

nanocomposite is illustrated in Figure 6, too. PDs concentrate on the layered silicates and shift toward polymer regions because charge has been built up on the surface of the layered silicates. PDs crawl selectively into the amorphous regions that are less resistant against PD than spherulite regions.

Nevertheless, it is still uncertain how PD resistance will be affected by nanometric spherulites and /or “interaction zones” around nanofillers.

Results obtained are summarized as follows:

- (i) Polyamide nanocomposites exhibited much stronger PD resistance than pure polyamide.
- (ii) Surface erosion due to PD was 5 times shallower for polyamide nanocomposites than for pure polyamide under a certain condition.
- (iii) High PD resistant layered silicate is considered to play a significant role in PD resistance of PA/layered silicate nanocomposite.
- (iv) Roles of spherulites and interaction zones remain still unsolved.

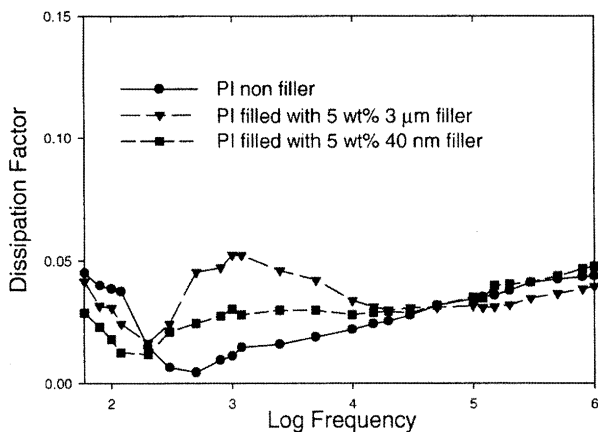


Figure 7. Frequency dependence of dissipation factors for polyimide without fillers, and with 5 wt% 3 μm microfillers and 5 wt% 40 nm nanofillers [9].

4.2 ELECTRICAL CONDUCTION IN POLYIMIDE/SILICA NANOCOMPOSITES [6]

Thermosetting polyimide with 2–10 wt% nanofillers were prepared by the solvent cast method. Silica was used as nanofillers. Their size was estimated to be 40 nm. Polyimide films were cured into free standing films of approximately 25 to 50 μm in thickness. Aluminum electrodes of 1.27 cm in diameter were deposited onto both surfaces of the films by sputtering prior to electrical tests. The electrical properties of polyimide-based nanocomposites were investigated by several ways such as isothermal steady state current, dielectric spectroscopy, and thermally stimulated current measurements.

The effect of nanofillers on the dielectric properties was evaluated via interfacial polarization and electrical conduction mechanism investigation. As shown in Figure 7, polyimide with micrometer size (3 μm) fillers has a loss peak at about 1 kHz, while pure polyimide has no peak around the frequency. This peak is attributed to the Maxwell-Wagner interfacial polarization. This peak is much reduced for nanocomposites with 40 nm fillers. The reduction of interfacial polarization was explained in terms of the field mitigation with the reduction of filler dimension.

The electrical conduction of polyimide nanocomposites was found to be fairly consistent with the space charge limited current (SCLC) mechanism. Polyimide with 2 wt% nanofillers showed some reduction in bulk electrical conductivity compared to pure material and 10wt% microfiller polyimide at elevated temperatures. Thermally stimulated current (TSC) peak shifted from 185°C to 200°C or higher temperatures. Results obtained are summarized as follows:

(i) Peak dissipation factor of PI nanocomposite was smaller at 1 kHz than that of PI microcomposite.

(ii) dc current of PI nanocomposite was smaller at high temperatures than that of pure PI and PI microcomposite.

(iii) A TSC peak shifted from 185°C for pure PI to 200°C or higher temperatures for PI nanocomposite.

The first phenomenon was understood in terms of interfacial polarization. The second and third phenomena were correlated to the introduction of deeper carrier traps. It was emphasized that the nature of such traps and the interaction between filler and matrix would deserve further investigation.

4.3 THERMAL AND MECHANICAL PROPERTIES OF POLYIMIDE NANOCOMPOSITES [11]

Commercially available nanoparticles were dispersed evenly into standard thermosetting polyimide enamel after proper surface treatment or coating of nanoparticles. Nanoparticles of 40 nm in thickness were added by 1 to 10wt%. All the materials were solvent cast and cured into free standing films of approximately 50 to 100 μm in thickness. Tensile strength, scratch hardness and thermal conductivity were measured for these films. By focusing on the relationship between nanoparticles and polymer matrices inside nanocomposites, the following were obtained:

(i) Elongation and strength to failure improved if PI was converted into PI nanocomposite.

(ii) Scratch hardness of PI nanocomposite was larger than that of PI microcomposite.

(iii) Tensile modulus of PI nanocomposite showed no significant change between pure PI and PI nanocomposite.

(iv) Thermal conductivity was enhanced for PI nanocomposite filled with coated nanoparticles as compared to pure PI and PI microcomposite.

Surface modification or coating effect of the above statement (iv) was found to increase thermal conductivity as shown in Figure 8. It is interesting to cite that surface treatment of nanofillers seemed to improve the thermal conductivity of PI nanocomposite, which indicated that filler-matrix interactions functioned for performance improvement. It was emphasized that polymer chains would interact with the surface of nanofillers to alter various properties such as crystallinity, cross-link density, mobility and conformation to change mechanical and thermal properties in the end.

4.4 ELECTRICAL PROPERTIES OF POLYMER NANOCOMPOSITES BASED UPON ORGANOPHILIC LAYERED SILICATES [12]

Ethylene/vinylacetate (EVA) and isotactic polypropylene (iso-PP) nanocomposites were prepared from organophilic layered silicates. Synthetic fluorohectorite was modified by means of cation exchange of their interlayer

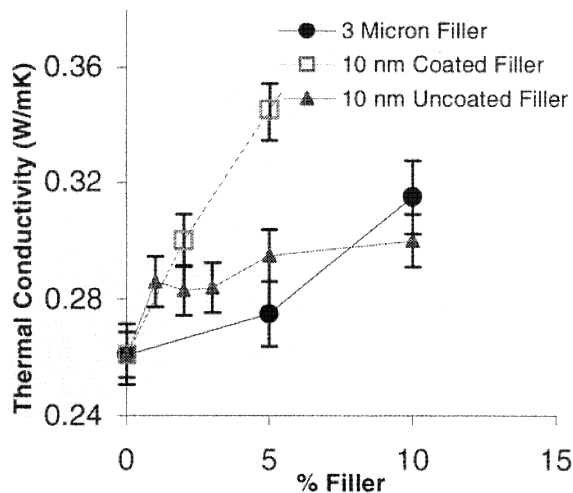


Figure 8. Thermal conductivity vs. filler content characteristics for pure PI, PI microcomposite, and PI nanocomposites (nanoparticles uncoated and coated) [10].

sodium cations for hydrophobic alkyl ammonium cations in order to expand the interlayer distance and to facilitate intercalation and exfoliation during processing. Non-polar polymers such as iso-PP needed compatibilizers and high shearing stress during processing, while polar polymers such as EVA did not. In case of iso-PP, the addition of maleic anhydride grafted PP promoted exfoliation and in-situ formation of nanocomposites

Fluorohectorite, modified by means of cation exchange with protonated octadecylamin (ODA), was used as nanofillers with different concentration, i.e., 2, 3 and 6 wt%. Specimens used were prepared in a two step process. In the first step, the iso-PP (PP HC 001 A-B1 from Borealis) was melt-blended in conjunction with the PP-g-MA compatibilizer (Licomont AR 504 from Clariant) and the organohectorite (Somafif ME 100 from CO-OP Chemical Japan), modified via ODA cation exchange, using a corotation twin-screw extruder (Collin; ZK 25T) at a temperature of 220°C. Similar procedure was used to prepare EVA (ESCORENE ultra UL 00012 from Exxon Chemicals) nanocomposites. In the second step, nanocomposite films were prepared using the same extruder with a chill roll unit (Collin; CR 72T). Obtained films were as thick as about 400 μm. Nanofillers in the films were checked by TEM.

Space charge, conduction current and dielectric strength measurements were performed for polymer nanocomposites described above. The comparison among unfilled and nanofilled materials, with different filler concentrations, showed that space charge accumulation phenomena were considerably affected by the presence of nanofillers. Results are summarized as follows:

(i) Space charge decreased at medium high electric field by introduction of nanofillers for EVA and PP, while it increased at low fields.

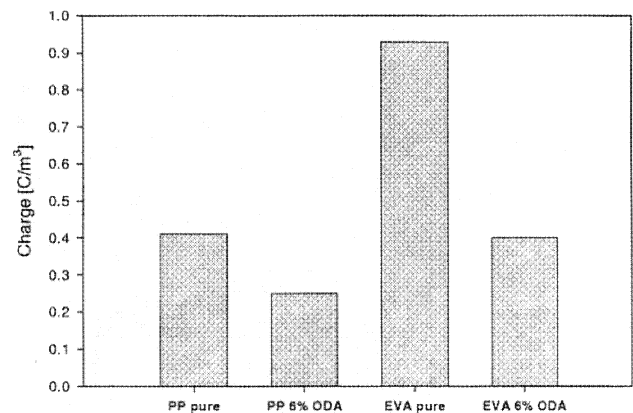


Figure 9. Comparison of space charge values at poling field of 40 kV/mm for EVA and PP (base and nanofilled 6 wt%) [11].

(ii) Space charge inception threshold shifted to lower values (e.g. from 14 to 5 kV/mm for PP) for both EVA and PP, if nanofillers were added. It decreased if nanofiller content increased.

(iii) Depolarization charge was faster in its decay rate for nanocomposites than for base EVA and PP. Especially PP with 6 wt% ODA showed a marked fast decay rate.

(iv) dc conduction current increased for nanocomposites.

(v) dc breakdown strength increased for nanocomposite PP, while it did not change significantly for EVA

Space charge accumulated at a probable design stress such as 40kV/mm was found to be smaller for nanocomposites than for pure or base polymers, as shown in Figure 9. This deviation was more evident as nanofiller content increased up to a level of about 10%. Further increase of nanofiller concentration worsened electrical properties. It was considered from space charge characteristics, depolarization and dc current measurements that ionic carriers were available and that carrier trap distribution was significantly modified likely due to introduction of shallow traps.

Some apparent contradiction should be pointed out as for dc current for future investigation. Namely dc current decreased, when some nanofillers were added to PI, as the reference [9] indicated, while increased when layered silicates were dispersed in EVA and PP, as in reference [11]. In both papers [9] and [11], ionic carriers and carrier traps were proposed for electrical conduction, but it was not revealed whether the traps were associated with ionic conduction or electronic conduction.

4.5 EPOXY WITH METAL-OXIDE FILLERS [13]

Titanium dioxide (TiO₂) micro (1.5 μm) fillers and nanofillers (38 nm) were dispersed in Bisphenol-A epoxy (Vantico CY1300 + HY956). Such composites were mechanically stirred and molded into films of 500 to 750 μm

in thickness. In case of nanofiller dispersion, the composites were subjected to large shear force in the mixing process to obviate unwanted clustering or agglomeration of nanofillers (it was pointed out that nanoparticles would tend to agglomerate to make dispersion in resins quite difficult). For most electrical characterization, the cast films with 1, 10 and 50 wt% micro- and nano-particles were provided with evaporated 100 nm aluminum electrodes. Results can be summarized as follows.

(i) Glass transition temperature (T_g) decreased or remained unchanged when an epoxy resin was filled by nanocomposite particles, while T_g increased when it was microcomposited.

(ii) Permittivity and loss tangent exhibited different characteristics depending on voltage frequency and temperature.

(iii) Space charge behaved in a similar way as the base resin for nanocomposites, while substantial space charge was generated internally for microcomposites.

(iv) Decay of charge in nanocomposites was very rapid.

It was stated from T_g data that nanoparticles might behave in a similar way to filtered plasticizers rather than as "foreign" substances creating a macroscopic interfaces. Dielectric spectra were virtually indistinguishable between microcomposites with 10 wt% particulates and the base resin in the low frequency range, because only the charge at the electrode was involved. On the contrary, a marked difference was observed at low frequencies and high temperatures between base resin and nanocomposites with 10 wt% nanofillers. The nanocomposites showed a flat $\tan \delta$ response at low frequencies. In addition to (iii), the decay of charge was very rapid in nanocomposites compared to microcomposites. It was emphasized from the above results and some consideration that nanometric fillers would mitigate the interfacial polarization characteristic of conventional materials with a reduction in the internal field accumulation. Hypothetical "interaction zone" was defined here as a short-range highly immobilized layers that might develop near the surface of nanofillers to explain major phenomena observed in nanocomposites. This will be discussed later.

The continuation of the same research, [14], considered uniform field breakdown (BDV) specimens, prepared by the use of a mold having multiple spherical protrusions so as to form a plurality of recessed specimens in one operation. Divergent filed specimens used for electrocluminescence (EL) measurements were created by molding around electrolytically etched tungsten needles having a well-characterized tip radius of about 4 μm . Lamina molded specimens were subjected to thermally stimulated current (TSC) measurements. Experimental results are as follows:

(i) BDV remained almost same up to 10% nanoparticle loading, while it decreased significantly for 10% microparticle loading.

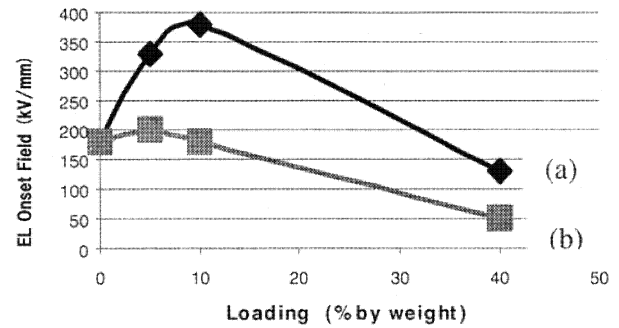


Figure 10. Electroluminescence onset field as a function of TiO_2 loading, a, 38 nm; b, 1.5 μm [13].

(ii) EL onset field was higher for nanocomposites than for base resins and microcomposites.

(iii) The α -TSC peak seemed to shift upward in temperature for nanocomposites. Microcomposites exhibited a significant ρ -TSC peak of interfacial polarization above 100 $^\circ\text{C}$, while nanocomposites had no peak at all.

As shown in Figure 10, EL onset field was a function of filler loading with a peak at 10wt% loading for nanocomposites. Based on experimental results obtained above, interfacial space charge or interfacial polarization was considered crucial and was associated with Maxwell-Wagner effect. Then, it was emphasized that nanoparticles might mitigate effects of trapped entanglement on the Maxwell-Wagner effect.

4.6 STUDY OF THE PROPERTIES OF RTV NANOCOMPOSITE COATINGS [15]

Specimens used for tracking tests were prepared and divided in three groups, that consisted of Group 1 (virgin room temperature vulcanized silicone rubber, i.e., RTV), Group 2 (RTV filled with 40 wt% ATH) and Group 3 (RTV with 5 wt% layered silicate nanocomposite). Surface SEM observations confirmed that layered nanosilicates were randomly exfoliated and dispersed in RTV. It was considered that layered nanosilicates were covered with organophilic cations when pristine layered silicates were processed by intercalation, so that the surface energy of normally hydrophilic silicates was lowered to make layered nanosilicates compatible with RTV coatings. Specimens of 120 mm \times 50 mm \times 6 mm in size were subjected to a standard tracking test. As shown in Table 6, the addition of nanoparticles to RTV silicone rubber improved their tracking performances comparable to that of ATH filled RTV. In addition to that, the maximum erosion depth was much smaller for RTV nanocomposites than for virgin RTV and ATH filled RTV. Experiments confirmed a slight increase of $\tan \delta$, a slight decrease of ϵ_r and a little change of ρ_v .

Table 6. Tracking performance of RTV, ATH filled RTV and RTV nanocomposite.

| | Tracking voltage (kV) | Speed of conducting solution (ml/min) | Endurance time (min) | Maximum erosion depth (mm) |
|------------|-----------------------|---------------------------------------|----------------------|----------------------------|
| Virgin | 2.5 | 0.15 | 180 | 3.9 |
| 40 wt% AHT | 3.5 | 0.3 | 360 | 4.9 |
| 5 wt% LS | 3.5 | 0.3 | 360 | 1.4 |

Results are summarized as follows:

(i) Flame retardation of RTV/layered silicate nanocomposite was highly improved.

(ii) The needed amount of nano-layered silicate was only about one tenth of that of the conventional ATH filler.

(iii) Properties such as $\tan \delta$, ϵ_r and ρ_v remained, after the addition of the nanofiller, satisfactory.

4.7 EFFECT OF SPACE CHARGE IN NANOCOMPOSITE OF LDPE/TiO₂ [16]

Low-density polyethylene (LDPE)/ TiO₂ nanocomposites were prepared by the solution blending method using nanoparticles of TiO₂ (purity: 99.5 % or larger, average diameter 30 nm, specific surface $150 \pm \text{m}^2/\text{g}$, loose density: 0.05–0.06 g/cm³). Detailed procedure is described in literature [12]. Specimens for experiments were 30 μm in thickness. The disperse performance of TiO₂ in LDPE was observed with the scanning electron microscope (SEM). TiO₂ was dispersed uniformly in LDPE up to 5wt% through controlling temperature and content of the solution of LDPE; the largest conglomeration diameter of TiO₂ in LDPE was less than 80 nm. Space charge distribution of such specimens with and without nano TiO₂ was measured by the pulsed electroacoustic (PEA) method. The following results were obtained:

(i) Hetero-polar space charge near electrodes was much less in LDPE/ TiO₂ nanocomposites than that in pure LDPE under lower direct current (dc) stress (no more than 40 kV/mm).

(ii) Space charge inside the nanocomposites was much more uniform than that in pure LDPE. Thus electrical stress concentration was improved under dc stress in the nanocomposites.

(iii) Decay rate of the remnant of space charge in LDPE specimens containing TiO₂ increased with increasing of the TiO₂, when short-circuited after pre-stress at 50 kV/mm for 1 h.

4.8 EFFECT OF α AND γ PHASE NANO Al₂O₃ ON MECHANICAL PROPERTIES OF EPDM [17]

Nano Al₂O₃ in α and γ phases was mechanically blended with sulphurized agent (dicumyl peroxide or DCP: 2 wt%) and 1010 type of antioxidant (0.2 wt%) into ethylene-propylene-diene methylene linkage rubber (EPDM). Both kinds of compounds were cross-linked and molded into specimens under the same conditions. SEM observations indicated that Al₂O₃ in γ phase was dispersed more uniformly than Al₂O₃ in α phase. The following results were obtained:

(i) Tensile strength and elongation of EPDM containing nano Al₂O₃ in γ phase were better than those of EPDM containing nano Al₂O₃ in α phase.

(ii) The smaller diameter of the Al₂O₃ nanoparticles gave the larger improvement in mechanical properties.

(iii) Surface pretreatment of Al₂O₃ nanoparticles helped improve the mechanical properties.

4.9 SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE/SILICA NON-CLUSTERED COMPOSITES [18]

A new class of PD (partial discharge) resistant films made of “nanocluster-trapped” polyimide (PI) /silica (SiO₂) nanocomposites that were synthesized by the sol-gel reaction was obtained by hydrolysis and poly-condensation of tetraethoxysilane (TEOS ceramic precursor) or methyl-triethoxysilane (MTEOS ceramic precursor) in the solution of polyamic acid (PAA) dissolved in N,N-dimethyl-acetamide (DMAc), followed by heating. Some more detailed description is given in literature [17]. The chemical surface and the surface morphology of the composite films were characterized by using Atomic Force Microscope (AFM) and Fourier Transform Infrared Spectroscopy (FTIR). Size of silica particles ranged from 127 to 506 nm, and MTEOS gave smaller sizes than TEOS. PD resistance of the composite films was tested under high voltage using rod-plate electrode to derive PD lifetime. As shown in Figure 11, PD lifetime increases with the increase of silica content based on MTEOS. The same behavior was shown by TEOS, with life increasing almost linearly with silica content. PD lifetime was longer for MTEOS than for TEOS. Therefore, life was considered to be affected not only by the type of precursor, but also by agglomeration extent of inorganic particles. The results obtained are summarized as follows:

(i) PD resistance was larger for PI/silica nanocomposites than for pure PI specimens.

(ii) Both agglomeration of particles and the type of precursor seemed to affect PD lifetime.

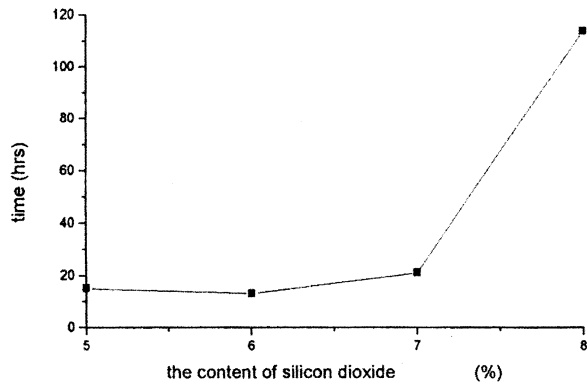


Figure 11. PD lifetime vs. silica content for MTEOS PI/silica composite [17].

4.10 PD-RESISTANCE OF POLYIMIDE NANOCOMPOSITES [19]

Specimens same as those used in the paper [18] were prepared. Nanocluster-trapped PI /silica composites [18] were renamed as polyimide-nano inorganic composites in [19]. Particle size was presumed to be in the range 127 to 506 nm. PI nanocomposite films were subjected to surface partial discharges according to IEC-343 and ASTM-2275. PD breakdown time was measured for 30 μm films. PD breakdown time was 3-12 times longer for nanocomposite PI than for pure PI. Silica loading was optimum at 8 wt% for PD resistance. Dielectric spectroscopy, such as C_p - ω and $\tan \delta$ - ω characteristics, was investigated both before and after PD aging, and the surface morphology was char-

acterized by AFM. Dielectric spectroscopy data were obtained at 0, 30, and 45 minutes of aging time. Results regarding capacitance were uncertain. Permittivity and the peak value of $\tan \delta$ decreased steadily as aging time increased, while the frequency at $\tan \delta$ peak shifted upward from 1.16 to 1.27 MHz for pure PI and from 0.67 to 1.99 MHz for nanocomposite PI.

The following results were obtained:

(i) PD resistance was stronger for nanocomposites than for pure PI.

(ii) Silica loading of 8 wt% gave the best PD resistance.

(iii) Capacitance at $\tan \delta$ peak in the frequency dependence decreased with aging time (from 169 to 179 pF and from 194 to 274 pF).

(iv) The frequency corresponding to the peak value of $\tan \delta$ shifted to higher values as aging time increased.

(v) Such frequency shift was larger (from 0.67 to 1.99 MHz) for nanocomposite PI than (from 1.16 to 1.27 MHz) for pure PI.

4.11 EPOXY-ORGANICALLY MODIFIED LAYERED SILICATE NANOCOMPOSITES [20]

Epoxy-silicate nanocomposites were prepared by dispersing synthetic layered silicates modified with alkyl-ammonium ions in an epoxy resin (diglycidyl ether of bisphenol-A, DGEBA, Epikote 828, epoxide equivalent weight = 184 to 194 or diglycidyl ether of bisphenol-F, DGEBF, Epikote 807, epoxide equivalent weight = 160 to 175, Japan Epoxy Resin Co.). Two kinds of organically modified silicates (STN and SEN) provided by Co-op Chemical Co. were used. In the dispersing process, the organically modified layered silicates were mixed in epoxy resin with shearing, and aggregations of the silicates were removed by centrifugal separation after mixing epoxy resin and silicates. Micrographs taken by transmission electron microscopy (TEM) indicated that the nanocomposites had a mixed morphology including both parallel silica layers (0.1–0.5 μm , 5–15 layers) and exfoliated silica layers (nano-scale dispersion) area. Epoxy nanocomposite with 3wt% DGEBA/SEN showed similar mechanical strength to that with 6 wt% DGEBA/STN. As shown in Figure 12, the permittivity and $\tan \delta$ were smaller for nanocomposite epoxy especially at high temperatures than for pure epoxy. Marked improvement was confirmed for $\tan \delta$ at temperatures above 120°C.

The following results were obtained:

(i) A glass transition temperature (T_g) of the nanocomposite shifted to a higher temperature (+ 20°C) than pure epoxy.

(ii) Mechanical strength improved by layered silicate addition (3 to 6 wt%).

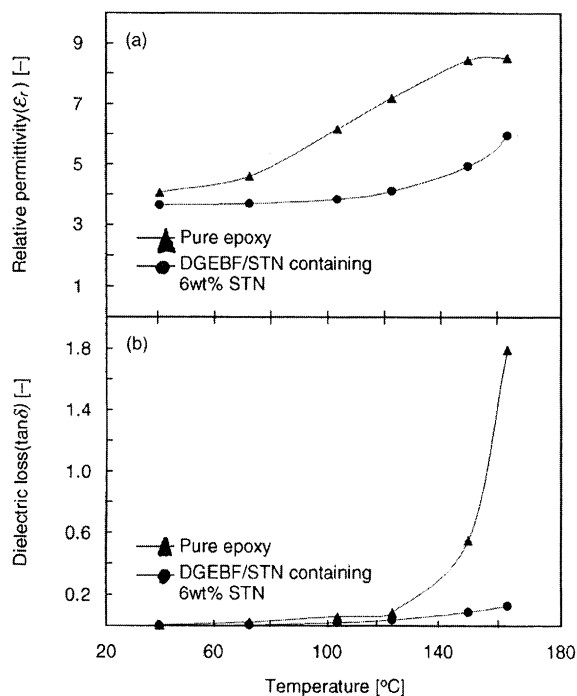


Figure 12. Temperature dependence of permittivity and $\tan \delta$ for pure and nanocomposite epoxy resin [19].

(iii) Permittivity and $\tan \delta$ were smaller for nanocomposite epoxy than for pure epoxy.

(iv) Dispersion of modified silicate prevented relative permittivity (ϵ_r) and dielectric loss ($\tan \delta$) from increasing at high temperatures above the glass transition temperature.

4.12 CO-CONTINUOUS NANOSTRUCTURED POLYMER BY REACTIVE BLENDING [21]

Polymer blends consist of a particulate minority phase dispersed in a matrix. There are several methods to blend two homopolymers in continuous wt%: the “compatibilizer” method, and the block copolymer/homopolymer/homopolymer blend method. A stable co-continuous copolymer was obtained on the basis of the graft polymer blend method. Then, a nanostructured polyethylene (PE)-polyamide (PA) copolymer, especially with co-continuous morphology, was produced through a self-assembly process by reactive blending. PE and PA were functionalized to drive reactive blending. The functionalized PE used for the backbone chain was a random co-polymer of ethylene, ethylacrylate and maleic anhydride (MAH). PA6 synthesized by polycondensation, was terminated at one end by the reactive functional group NH_2 . It exhibited excellent mechanical properties over conventional PE and even classical PE/PA blends, as well as a nearly constant elastic modulus of 10 MPa between 100°C and 200 °C, high yield stress and high strain tensile behavior. It did not creep, when heated above the PE melting point.

Results obtained for mechanical properties of a new PE/PA blend are as follows:

- (i) It exhibited lower creep and greater heat resistance.
- (ii) It remained stable at much higher temperatures and was provided with better mechanical properties than classical blends.

(iii) This technology would point the way towards the design of stable co-continuous structure over a wide range of compositions and polymer types.

4.13 NEW EPOXY RESINS WITH CONTROLLED HIGH ORDER NANOSTRUCTURE [22, 23]

Epoxy resins with mono and twin mesogens were formulated. Mesogens were highly ordered in nanoscale through their self-assembly process, possibly resulting in improvement of thermal conductivity by reducing as it scattering. They would form nanometric liquid crystal regions that were 5 to 30 nm for mono mesogens, and in the range of 500 nm for twin mesogens. Thermal conductivity was obtained to be 0.33 W/mK for mono mesogens, and 0.85 – 0.96 W/mK for twin mesogens. These values should be compared to 0.17 W/mK for conventional epoxy. As shown in Figure 13, epoxy resins with nano-ordered structures were obtained to have better thermal conductivity than conventional epoxy resins.

Results obtained are summarized as follows:

- (i) Epoxy resins exhibited higher thermal conductivity, if mesogens were highly ordered in nanometric scale.
- (ii) Thermal conductivity was 5 times higher for epoxy resins with twin mesogens than for conventional epoxy resins.

High thermal conductivity epoxy explained in [19] was aimed at low thermal expansion and low water absorption, as well as high Young’s modulus even at high temperatures, for use in microelectronics printed circuit boards. Some other methods have even been developed to increase thermal conductivity of epoxy resins. One is to form smectic liquid crystal structure in epoxy by using large mesogens, and the other is to increase unidirectional ther-

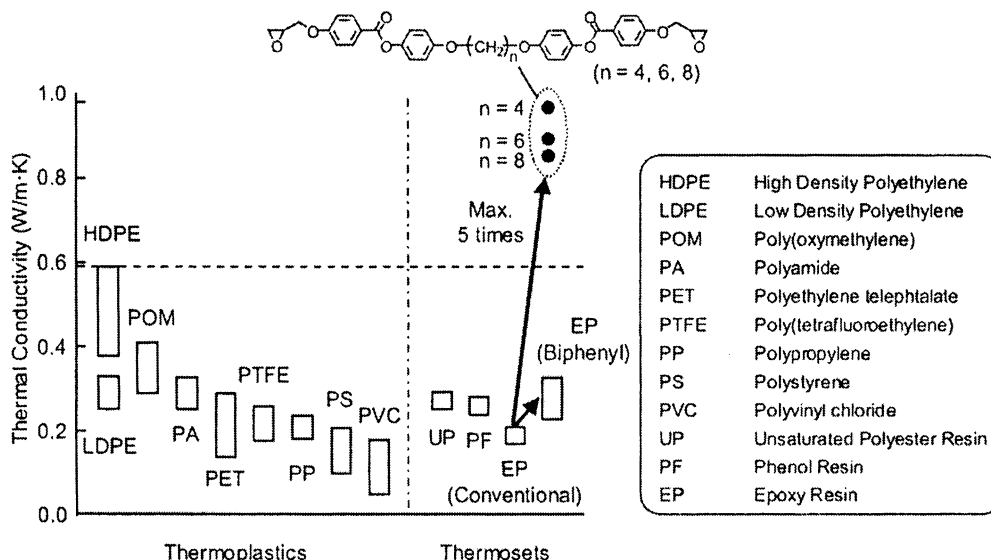


Figure 13. Thermal conductivity of various polymers for commercial use [21, 22].

mal conductivity by driving liquid crystal regions toward anisotropic orientation under high magnetic field, such as 10 Tesla.

5 DISCUSSION

5.1 DISCUSSION ON ELECTRICAL PROPERTIES

5.1.1 EFFECT OF NANOMIZATION ON PERMITTIVITY AND TAN δ

(i) Polyimide/silica nanocomposites [6], Irwin (GE):

Value of tan δ tends to decrease in the order of pure PI, PI/silica microcomposite and PI/silica nanocomposite at the low frequency region up to about 200 Hz between 60 Hz and 1 MHz. A peak appears at about 1 kHz in the middle frequency region (between 60 Hz and 1 MHz) in case of PI/silica microcomposite. This peak is reduced fairly much in case of PI/silica nanocomposites. The peak is ascribed to the Maxwell-Wagner interfacial polarization. This reduction might be caused by the mitigation of the field around fillers due to size difference.

(ii) Epoxy/TiO₂ nanocomposites: Permittivity [13], Nelson (RPI):

Above 50 or 60 Hz, the dielectric spectra are virtually indistinguishable among base epoxy, epoxy microcomposite and epoxy nanocomposite. This very low frequency process might not be due to particulates in bulk, but to charges at the electrodes. The microcomposite material exhibits two peaks of tan δ that are observed at very low frequencies, such as 8 mHz and 100 mHz at two different high temperatures for the microcomposite, respectively. Values of tan δ at intermediate frequencies, around 100 Hz, are smaller for nanocomposite than for microcomposite. This trend is similar to the data [9] obtained for PI/silica composite. This might be related to the function of nanofillers to immobilize polymer chains in what are called "interaction zones".

(iii) RTV silicone rubber/ layered silicate nanocomposites: [15] Lan (Wuhan)

Nanocomposites exhibit a slight increase of tan δ and a slight decrease of ϵ_r at the commercial frequency. No digital data are available as for tan δ , although some figures are given.

(iv) PI/silica nanocomposites: [19], Lei (Harbin)

Nanocomposite PI gives lower permittivity than pure PI in the frequency region between 100 kHz and 10 MHz. (Note: This appears to be contradictory to the corresponding figures.)

(vi) Epoxy/layered silicate nanocomposites: [20], Imai (Toshiba)

Permittivity and tan δ are smaller for nanocomposite epoxy than for base epoxy.

Interpretation of dielectric spectra seem to be complicated when comparing base resin, microcomposites, and nanocomposites. It is questionable whether or not the permittivity and tan δ are reduced by nanomization at the commercial frequency. Some data indicate a certain reduction, but some other data do not, resulting in apparent contradictions. This may depend on the way nanofillers interact with companion polymers. These results require further investigation, considering also methods of dispersing fillers in polymer matrices. It is certainly crucial to prevent nanofillers from agglomeration or to disperse fillers homogeneously in polymer matrices for obtaining reproducible and reliable data.

5.1.2

dc ELECTRICAL CONDUCTIVITY

(i) Polyimide/silica nanocomposites [6], Irwin (GE):

dc current at low field decreases at high temperatures by nanomization.

(ii) PP and EVA/layered silicate nanocomposites [12], Montanari (Bologna):

dc current at high field (30kV/mm) increases at room temperature by nanomization. Thus apparently opposite data were obtained. But this will depend on the modification of shallow trap depth levels introduced by nanomization.

5.1.3 SPACE CHARGE, TSC AND EL BEHAVIORS

(i) Space Charge

- Space charge increases at low field and decreases at high field due to nanomization – [PP and EVA/LS [12], Montanari (BLN)].

- Space charge inception field decreases due to nanomization [PP and EVA/LS [12], Montanari (BLN)].

- Space charge is generated internally by nanomization [Epoxy/TiO₂ [13], Nelson (RPI)].

- Charge decay time decreases due to nanomization [PP and EVA/LS [12], Montanari (BLN)].

Charge decay time decreases due to nanomization [Epoxy/TiO₂ [13], Nelson (RPI)].

(ii) TSC

- A TSC peak shifts toward higher temperatures due to nanomization [PI/Silica [6], Irwin (GE)].

- A TSC peak shifts toward higher temperatures due to nanomization [Epoxy/TiO₂ [14], Nelson (RPI)].

(iii) Electroluminescence

- EL onset field increases due to nanomization [Epoxy/TiO₂ [14], Nelson (RPI)].

Modification of trap depth distribution due to the introduction of nanofillers, particularly in reference to deep traps, might explain space charge, TSC and EL characteristics as described above. Fast charge decay and other space charge characteristics seem to be contradictory with the deep trap theory and certainly need some other consideration.

5.1.4 DIELECTRIC BREAKDOWN STRENGTH

- BDV increases for PP due to nanomization, while EVA decreases a bit [PP and EVA/LS [12], Montanari (BLN)].

- BDV remains same up to 10wt% loading, and tends to decrease for more loading [Epoxy/TiO₂ [14], Nelson (RPI)].

As indicated above, dielectric breakdown strength might not be greatly affected by nanomization under small loading of nanofillers and proper dispersion conditions. Favorable results are obtained in some cases.

5.1.5 PD RESISTANCE

- PD resistance improves due to nanomization [PA/LS [10], Kozako (Waseda)].

- PD resistance improves due to nanomization [PI/Silica[18, 19], Zhang (Harbin)].

It would be probable that nanomization improves PD resistance of polymers, which certainly depends on how nanofillers are dispersed in polymer matrices and are compatible with them.

5.1.6 TRACKING RESISTANCE

- Flame retardancy improves due to nanomization [RTV/LS[15], Lan(Wuhan)].

5.2 RELATED PROPERTIES

5.2.1 GLASS TRANSITION TEMPERATURE

- T_g decreases or remains unchanged due to nanomization [Epoxy/TiO₂ [13], Nelson (RPI)].

- T_g increases due to nanomization [Epoxy/LS[20], Imai (Toshiba)].

It is possible to increase T_g by nanomization. It should be noted that it would require homogeneous dispersion of nanofillers for that purpose.

5.2.2 THERMAL CONDUCTIVITY

- Thermal conductivity enhances due to nanomization [PI/Silica [11], Irwin (GE)].

- Thermal conductivity enhances by introduction of nanometric liquid crystal polymers [Epoxy/nanoLC polymer [22, 23], Takezawa (Hitachi)].

Nanoparticles and nanometric crystal parts have higher thermal conductivity than base polymers, so that mixtures might be more thermally conductive than the base resins. It was suggested that “interaction zones” might have as good heat transfer as possible.

6 CONCLUSION

Polymer nanocomposites could be advantageous over traditional filled polymers in electrical and thermal properties as well as mechanical properties from the standpoint of dielectrics and electrical insulation. This feature will technologically result in compact design of electrical equipments with high reliability and thereby in significant cost reduction for system integration and maintenance. Since this feature is originated from mesoscopic characteristics of interaction zones between polymer matrices and nanofillers, it will open a new academic arena for dielectric and electrical insulation that will need quantum mechanics as well. Such interaction zones might be related to free volume and charge carrier trap distribution (shallow and deep traps), which should be further explored. In order to obtain excellent but low-cost polymer nanocomposites, existing material processing technologies should be more advanced so as to match dielectrics and electrical insulation. Results are summarized as follows:

6.1 EFFECTS OF NANOMIZATION

(1) dc conductivity increases and decreases depending on measurement conditions. Introduction of deep traps are suggested.

(2) Interfacial polarization can be reduced compared to microcomposites.

(3) There seems to be a certain reduction of permittivity due to nanomization. But change of permittivity as well as $\tan \delta$ is complicated, and not conclusive. Manufacturing processes should be more investigated for homogenous dispersion of nanofillers.

(4) Space charge, TSC and EL also give complex results in their threshold field and quantity. Introduction of additional levels of shallow and deep traps, as well as increase of trap density, might be involved. These might be deeply related to “interaction zones”. It is therefore necessary to characterize the interaction zones between nanofillers and polymer matrices chemically and physically.

(5) PD and tracking resistance improve. It is most probable. Role of nanofillers and interaction zones should be more clarified.

(6) Thermal conductivity and glass transition temperature could be increased by proper methods.

6.2 PROPERTIES OF POLYMER NANOCOMPOSITES

(1) Electrical and thermal properties as well as mechanical properties could be improved by nanomization of poly-

mers. Polymer nanocomposites are advantageous over conventional filled polymers, because a small amount of nanofillers might not modify the characteristics of base polymers considerably.

(2) Intercalation methods, sol-gel method, molecular composite formation method and nanofiller direct dispersion method are the major processing technologies, and should be more developed for better and cheaper materials with excellent interaction zones.

(3) Polymer matrices, nanofillers, and interaction zones between them are three major parts of nanocomposites. Their respective roles should be investigated based on material characteristics of interest.

(4) Especially interaction zones should be characterized chemically and physically.

(5) Deep and shallow traps should be investigated and correlated with physical and chemical characteristics of interaction zones. Especially a theory for trap level and density modification should be established.

(6) Interaction zones are mesoscopic in nature. This will open a completely new aspect of dielectrics and insulation studies, which need consideration based on quantum and statistical mechanics, too.

(7) Heat resistant thermoplastic nanocomposites are environmentally benign because of their recyclability. These could replace thermoset resins that cannot be recycled.

(8) Biodegradable polymers such as polylactic acid can be filled with nanofillers. PLA nanocomposites are expected to be used for eco-friendly electrical insulation.

7 APPLICATIONS

(1) Polymer nanocomposites have been investigated for future use of electrical insulation for power apparatus, power cables, outdoor insulators, and insulated wires for electric power technologies as well as printed circuit boards for electronics.

(2) Insulation could be more compact by using polymer nanocomposites, resulting in overall cost reduction in apparatus and installation.

(3) Reliability could be improved by using polymer nanocomposites, resulting in lower maintenance cost.

(4) Polymer nanocomposites will give much innovation in dielectric and insulation technologies.

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