Preparation and Thermal Conductivity of Polymer Nanocomposites

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Abstract. Polymer nanocomposites have attracted extensive research interest because of their unique properties, and will become one of the hotspots in the field of material research in the future. It partly overcomes the defects in the performance of single materials and traditional composites, so that the materials have both the advantages of inorganic materials (such as rigidity, high thermal stability and special optical and electromagnetic properties) and the advantages of polymer materials (such as elasticity, dielectric, ductility and processability). Moreover, because inorganic particles are uniformly distributed in the form of nanoparticles in the polymer body, Therefore, this kind of nanocomposites often have some special applications in the fields of mechanics, heat, electricity, optics, nonlinear optics and so on.

Keywords: high polymer · Nanocomposites · Thermal conductivity

1 Introduction

Due to its unique properties, polymer organic/inorganic composites have attracted extensive research interest and become one of the hotspots in the field of materials research. As a kind of important commercial materials, polymer composites have a wide range of applications, such as rubber elastomer barrier, electronic insulating materials, conductive and thermal conductive materials and some high-performance composites needed in the aerospace field. In order to prepare a kind of composite materials with special properties (such as barrier, reinforcement, toughening, conductivity, high refractive index, etc.), it can be designed from the properties of organic and inorganic materials. For example, a kind of composite material with certain toughness, hard plastic and light weight can be prepared by adding carbon fiber with high modulus but certain brittleness into the plastic polymer body with low modulus [1]. In recent years, the traditional micron size polymer composites can not reach an ideal and optimal balance in product performance, which hinders the further application and development of this kind of polymer composites. For example, high modulus organic-inorganic micron composites often have poor toughness, and the solution of toughness problem often needs to sacrifice the light transmission performance of the material [2]; In addition, when the polymer body contains high or low content of micron inorganic filler, micron size defects will lead to the overall fracture and yield of the material.

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In order to improve the limitations of traditional composites, the research and application of nanocomposites are developing vigorously. The so-called polymer nanocomposites refer to the uniform distribution of inorganic particles in the form of nanoparticles in the polymer matrix. Nanoparticles refer to that the size of the particles is less than 100 nm on at least one-dimensional scale. This kind of composite material overcomes the defects in the performance of single material and traditional composite material, which makes the material not only have the advantages of inorganic materials (such as rigidity, high thermal stability and special optical and electromagnetic properties), but also have the advantages of polymer materials (such as elasticity, dielectric, ductility and processability) [3]. Moreover, due to the uniform distribution of inorganic particles in the form of nanoparticles, this kind of nanocomposite material often has the advantages in electricity, optics Some special applications in the fields of Optoelectronics and nonlinear optics. In the development of polymer nanocomposites, although some polymer nanocomposites filled with carbon black and sintered silica have been used for nearly a century, the research and application in this field are still developing rapidly in recent years.

2 Related Work

2.1 Overview of Nano Materials

Nano materials are an important part of nano science. "Nano" comes from the Greek word "nanos", which means "tiny". It is a unit of length measurement. Strictly speaking, the size of nano materials, grains or particles is in the nano scale range (1 ~ 100 nm) in at least one dimension of three-dimensional space, or materials with nano materials as basic units. Nano materials and the corresponding developed nano technology are recognized as the most promising research and development field in the 21st century. Scholars will strive to develop new nano materials and new products with various excellent properties [4].

There are many kinds of nano materials and various classification methods. The following are some of the most common classification methods. ① According to the chemical composition of the material, it can be divided into: metal nano materials (such as nano copper), ceramic nano materials (such as nano alumina), glass nano materials (such as nano silicate), polymer nano materials (such as nano polypyrrole) and nanocomposites (such as nano stilbene/iron oxide composite); ② According to the scale of nano materials in three-dimensional space, it can be divided into: the three-dimensional spatial scale of materials is in the range of nano scale - 0 dimension (such as nanoparticle materials), two dimensions in the three-dimensional scale of materials are in the range of nano scale, and the length is significantly greater than the width - 1 dimension (such as nanotubes) and the spatial three-dimensional scale of materials. Only one dimension is in the range of nano scale, and the thickness is significantly less than the length and width - 2 dimensions (such as nano films); ③ According to the aggregation state of nanostructure units, the morphology can be divided into: nanotubes (such as manganese dioxide nanotubes), nanorods (such as copper oxide nanorods), nanowires (such as copper nanowires), nanospheres (such as titanium dioxide nanospheres), nanofilms (such as graphene films), nanoflowers (iron oxide nanoflowers), nanobelts (vanadium dioxide nanobelts) and nanoparticles (such as silicon dioxide nanoparticles) [5]. Several morphologies of nanoparticles are briefly given below, as shown in Fig. 1.

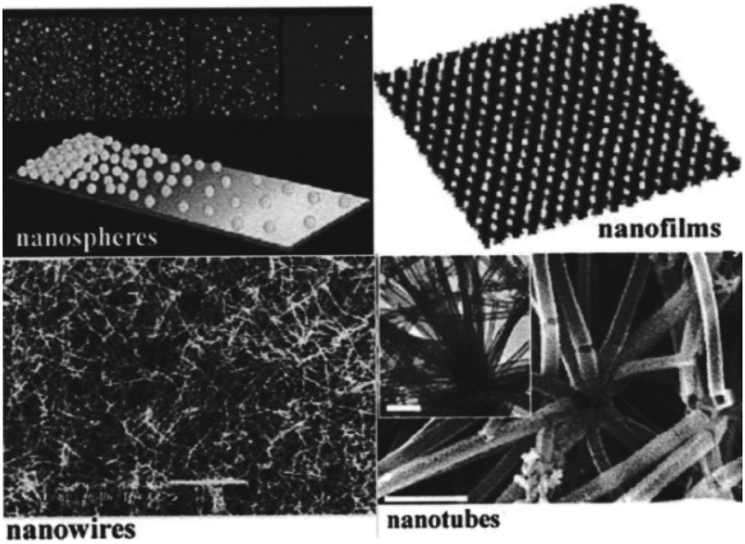

Fig. 1. Common morphologies of nano materials

2.2 Basic Effects and Properties of Nano Materials

Because the particle size of the material composed of nano materials has reached the nano scale, the specific surface area and the number of surface atoms of nano particles increase sharply. With the decrease of the particle size, its surface tension and surface energy increase rapidly, and the interaction force between the atoms of the material will also change. Therefore, nano materials exhibit many effects, including small size effect, surface effect, quantum size effect, macro quantum tunneling effect, dielectric confinement effect, Coulomb blocking effect and quantum tunneling effect.

It is because of these basic effects that nano materials show that they have many unique properties. The following mainly lists several remarkable characteristics of nano materials: (1) magnetic properties due to the influence of small-size effect, the anisotropy of nano particles will decrease rapidly. When the anisotropy energy is reduced to be characterized by thermal motion energy, the magnetization direction of the material will no longer be fixed in a direction easy to magnetize, and the magnetization direction will show a sharp super fluctuation state, This state will lead to superparamagnetism [6]. For example, when the particle size of Fe3O4 nanoparticles is less than or equal to 16 nm, the material will become a nano material with superparamagnetism (i.e. superparamagnetic). Ludmila CF and others successfully prepared Fe3O4 @ aminocellulose nanocomposites in organic media by combining the synthesis of magnetic materials and surface coated aminocellulose polymerization, and comprehensively studied the superparamagnetism of the composites. (2) Optical properties the optical properties of nanoparticles are greatly affected by surface effect and quantum size effect. Under the influence of these two effects, nanoparticles even have new optical properties that are not possessed by objects of the same material. The following aspects mainly list the new optical properties of nanoparticles: ① the reflectivity of nanoparticles to visible light is reduced and the absorptivity is enhanced, which leads to the broadening of the absorption band of infrared visible spectrum. There is a strong absorption spectrum in the broadband, which is the characteristic of broadband strong absorption [7]. ② Compared with ordinary particles, the infrared absorption band of nanoparticles will move to the short wavelength direction, resulting in a "blue shift phenomenon". ③ With the decrease of the material size, the short wave side of the light-emitting band of nano materials gradually extends to the visible range, and a new luminescence phenomenon appears, which is the photoluminescence characteristic. (3) Electrical properties due to dielectric confinement effect and Coulomb blocking effect, the conductivity of nanoparticles changes significantly with the change of particle size. For example, as we all know, silver has very good conductivity and is an excellent conductor of electricity. However, when the particle size of silver nanoparticles is between 10 nm and 15 nm, its resistance suddenly increases and loses conductivity, becoming an insulator. The addition of a nano material with good conductivity can improve the conductivity of the composite.

3 Composite Materials

3.1 Nanocomposites

Composites are multiphase materials with new functions and properties synthesized by two or more materials with different properties (inorganic non-metallic materials, polymers, metal materials, etc.) according to various physical, chemical and comprehensive methods. Each basic material in the composite is combined according to the interaction force between materials (chemical bond, charge gravity, etc.), and each material plays its own excellent characteristics in the composite, so as to make the performance of the composite more superior and more widely used [8].

Nanocomposites refer to composite materials in which at least one phase is in the range of nano scale. According to different basic materials, nanocomposites can be divided into inorganic organic composites (manganese dioxide polypyrrole composites), inorganic inorganic composites (carbon nanotube ~ Iron Composites), organic organic composites (polyaniline polypyrrole nanocomposites), inorganic organic organic composites (cuprous oxide polyvinylpyrrolidone graphene nanocomposites), etc.

3.2 Preparation Method of Nanocomposites

The preparation methods of nanocomposites are extended from the preparation methods of nanocomposites. Many methods can be directly used to synthesize nanocomposites. The common synthesis methods are: ① surface modification method uses surface modifiers to change the hydrophilicity (lipophilicity) of the surface of nano materials or change the physical and chemical environment of nano materials, so as to change the positive and negative of their surface charges, so that the materials can be easily compounded with another material under atomic or molecular forces. For example, our laboratory uses L-lysine as a surface modifier to change the hydrophilicity of the surface of iron oxide nanotubes, and uses hydrochloric acid to adjust the pH value to change the positive and negative charge on the surface of copper oxide nanotubes; ② In situ polymerization is a method to prepare nanocomposites by directly adding polymer monomers into liquid reaction medium and polymerizing inside or on the surface of nano materials under the conditions of ultrasound or stirring. For example, Yang Si and others successfully prepared Fe3O4 carbon nanofiber composites by in-situ polymerization. The composites have strong adsorption capacity for organic pollutants in wastewater and show good magnetic separation performance. In addition, there are ③ hydrothermal method; ④ Organic and inorganic mutual filling method; ⑤ Electrodeposition, etc. [9].

Because various basic materials for synthesizing nanocomposites have their own unique properties, and they learn from each other after compounding, nanocomposites have the excellent properties of various basic materials at the same time, and even have new properties that basic materials do not have. These advantages can broaden the application range of nanocomposites in various fields. According to the literature, at present, a variety of nanocomposites have been successfully developed and have been commercially applied to the parts of automobiles, ships and electromechanical products, batteries, capacitor materials of energy storage systems and catalysts in the field of catalysis. Recently, nanocomposites are favored in the packaging industry because of their superior flame retardant properties. People are studying nanocomposites for packaging of food, drugs, precision mechanical parts, electronic and electrical components. There is no doubt that the application field of nanocomposites will be very broad and the development prospect will be bright in the future.

4 Structure and Properties of Polymer Nanocomposites

Because composites have variable structural parameters (composite degree, connection type, symmetry, scale, periodicity, etc.) that a single material does not have, changing these parameters can greatly change the physical properties of composites in a wide range; And there are many kinds of composite effects caused by the synergistic effects among the components of the composite. Therefore, the properties of polymer based nanocomposites are not only related to the structural properties of nanoparticles, but also related to the aggregation structure and synergistic properties of nanoparticles, the structural properties of polymer matrix, the interfacial structural properties between particles and matrix, and the processing and composite process. By adjusting the variable structural parameters of polymer based nanocomposites, Using its composite effect, the material can obtain the best overall performance in terms of physical function, chemical and mechanical properties. In terms of chemical properties, it mainly shows excellent catalytic performance: nanoparticles loaded on polymer substrate not only give play to the specific catalysis of nanoparticles, but also ensure their catalytic stability (polymer matrix prevents the agglomeration of nanoparticles). In terms of mechanical properties, the addition of nanoparticles can greatly improve the mechanical properties of materials: Toyota Central Research Institute of Japan, Yubu Research Institute and Institute of chemistry of Chinese Academy of sciences have done a lot of work in nylon 6/clay nano in-situ composites. It is found that the composites have excellent properties such as high strength, high modulus and high thermal deformation temperature. In terms of physical functions, on the one hand, due to the quantum size effect and interface effect of nanoparticles, on the other hand, due to the interaction between nanoparticles and the interaction between particles and polymer matrix, polymer nanocomposites are different from conventional composites in the functional fields of sound, light, electricity, magnetism, dielectric and so on. The conductive percolation threshold of nano metal particles and polymer composites is smaller than that of conventional composites. Adding semiconductor nanoparticles such as nano-TiO2, Fe2O3 and ZnO into the resin can obtain good electrostatic shielding and change the color of the material; The addition of nanoparticles into polymer matrix can control the refractive index of the composite system more freely and improve the third-order nonlinear coefficient [10]; The composite of nano oxide particles and polymers has good microwave absorption properties: the composite of nano Al2O3 particles and rubber can improve the dielectric and wear resistance of rubber; When the polymer matrix itself has functional effects, the coupling between nanoparticles and it can produce new properties. For example, the composites of nanoparticles TiO2, WO3 and polyaniline have photochromism. TiO2 nanoparticles are compounded into semiconductor polymer MEH-PPV. The TiO2 nanoparticle system can emit light through scattering and amplification and become a narrow spectrum solid polymer laser diode.

This paper mainly discusses the physical function effect of 0–3 (or 2) polymer nanocomposites, that is, the active component is the particles with the scale at the nano scale, and its effect plays a major role in the main properties of the composites. Therefore, it focuses on the influence of the aggregation structure and synergistic properties of nanoparticles on the properties of materials, as well as the formation mechanism of the aggregation structure of nanoparticles.

4.1 Aggregation Structure of Nanoparticles

The aggregation structure of nanoparticles describes the dispersion and distribution of nanoparticles in the polymer matrix. It is related to the surface properties of particles, matrix properties, processing technology and composite mode of composites, and directly determines the synergistic effect of particles. In the polymer matrix, nanoparticles can be ordered distribution, which usually means that the distribution of their positions has long-range periodicity (one-dimensional, two-dimensional or three-dimensional order, and compound multimode order), or disordered distribution. The common parameters used to describe its structural characteristics are geometric parameters, including particle size distribution, particle spacing and topological parameters, and describing the adjacent condition of particles. They may have definite values, or they may be described by a distribution function and give a statistical average, which is similar to the complex of nanoparticles and polymers.

The combination method is related to the processing technology. However, in the disordered distribution, there is a kind of aggregation structure, which can not be fully reflected by the above structural parameters, that is, fractal structure. Fractal is a theory to describe the characteristics of random architecture, which is divided into linear fractal and Nonlinear Fractal. Linear fractal structure has self similarity and scale invariance in a certain scale range, and has no characteristic length. It is often described quantitatively by fractal dimension. It can be divided into regular fractal and random fractal. Nonlinear Fractal can be divided into self affine fractal, self reflexive fractal and non square fractal. The description of structure is characterized by multiple dimensions. Fractal reveals the inherent regularity and scale invariance of a large class of random systems, which is common in composite systems. It is related to the fact that composites are usually formed in the nonlinear process far from the thermodynamic equilibrium state. The correlation function can be used to distinguish the fractal structure from the real disordered structure. In practical composite systems, it is often not enough to use only one fractal dimension to describe their complex structures. Multifractals should be introduced.

4.2 Synergistic Properties of Nanoparticle Systems

The aggregation structure of nanoparticles in the matrix is different (including order, symmetry, particle size distribution, particle spacing distribution function, fractal dimension and so on), and its synergistic performance is also different.

For the ordered aggregation (dispersion) structure of nanoparticles, the position of particles in the matrix constitutes a super structure with long-range periodicity. Controlling the periodic characteristics of this structure has a great impact on the resonance and interference effects of composites. Changing the symmetry of the particle system can adjust the physical properties of the composite. For example, the particles are dispersed in an isotropic uniform matrix with different refractive index. If it is a spherical particle, the composite is also isotropic; If it is needle shaped particles arranged in an orientation, the composite is anisotropic, birefringent and positive; If the particles are directionally arranged, the composite is anisotropic and negative. In addition, by controlling the distribution of particles, the particles are arranged in a gradient in the matrix, and the physical parameters of the composites also change continuously in a gradient, so as to obtain functionally gradient composites, which can have many special properties that conventional composites do not have.

For the random distribution of nanoparticles in polymer matrix, including fractal structure and non fractal structure, percolation and mean field theory are often used to discuss the electromagnetic behavior of the system. In the low frequency region, percolation theory can successfully describe the conductivity of DC and AC, and the scaling law is applied near the threshold; In the high frequency region, small particles have uncompensated surface charge, which leads to dipole response. There is a strong long-range dipole dipole interaction. Different forms of mean field theory can be used to describe the light (dipole) response. Further, the effects of quantum size effect of nanoparticles, wide distribution of particle size, shape and orientation of particles, absorption of protective layer on particle surface, particle agglomeration and other factors are considered. The fractal structure can be excited by a uniform field, and its dipole cooperative excited state is localized on the fractal body; Non fractal can only be excited by non-uniform field, and the eigenstates are nonlocal. Computer numerical simulation shows that the absorption of fractal aggregation structure of nano silver particles widens in the visible and infrared regions of the spectrum, while its non fractal structure shows absorption only in the narrow region of 350 nm ~ 450 nm. This is because for fractal bodies, the dipole dipole interaction is localized in the cell of fractal aggregates, and the cell has many different local structures and shows different resonance frequencies. For non fractal aggregates, the dipole dipole interaction extends to the whole sample and absorbs light only in a narrow spectral region.

5 Conclusion

From the perspective of materials, the progress of science and technology provides smaller and smaller sizes for materials with high precision and good performance. "Small" is not only beautiful but also very useful. When the size of the material is small to a certain order of magnitude, it is called "nano material". This material is located in the transition region between atomic clusters and macro matter. At present, researchers have used chemical and physical methods to involve nanotechnology in the synthesis of functional materials (size in the range of 1 nm to 100 nm) and various application fields. The nano size of materials determines the excellent physical and chemical properties of materials in molecular and supramolecular structures. Assembling nanostructures into ordered arrays is a necessary step to make nanomaterials functional and operable. Novel nanostructured materials and devices with high performance can be prepared by constructing and assembling nano individuals.

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