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Effect of Dispersion of Nano-inorganic Particles on the Properties of Polymer Nanocomposites

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Abstract. Nanocomposites refer to materials with at least one one-dimensional dimension within 100nm of the dispersed phase of the composite. Nanomaterials have a large phase interface area, which have many new physical and chemical properties that macroscopic objects do not have. The research on dispersing nano-particles in polymer to improve the properties of polymer materials was introduced in this paper, and the influencing factors of dispersing effect of nano-particles in polymer were studied from the aspects of surface treatment agent and mechanical processing technology and so on.

1. Introduction

Roy and Kormarneni et al.[1] first proposed the concept of nanocomposites in 1984, namely, materials with at least one one-dimensional dimension within 100nm of the dispersed phase of the composite. Because of the large interfacial area between the disperse phase and matrix phase of the nanocomposite material (such as the dispersed phase particle size of 1 ~ 20 nm, surface area as high as 160 ~ 640 m² / g), if we can combine the rigidity, dimensional stability and thermal stability of inorganics with the toughness, processability, and dielectric properties of polymer perfectly, the nanocomposites with excellent comprehensive properties will be received. CaCO₃ is a widely used inorganic filler. As inorganic nanoparticles can enhance and toughen polymers, many researchers are interested in it.

However, the ultrafine inorganic filled polymer materials prepared by the traditional blending method are far from the nano-dispersion level and only belong to the micro-composite materials. The reason is that when the particle size of the filler is less than 1 ~ 0.1μm, the particle surface energy is very large, and the self-aggregation between particles is very strong. On the other hand, the inhomogeneity of the mixture makes it difficult for the existing interfacial modification technology to completely eliminate the interfacial tension between the filler and the polymer matrix, so as to achieve the ideal interfacial adhesion. Therefore, the dispersion of nanomaterials in polymers to improve the properties of polymer materials has been a technical difficulty in this field, and also a research hotspot in recent years.

2. Properties of nanocomposites

In the toughening of plastics[2], organic elastomers (such as CPE, EVA, MBS, SBS, ACR, NBR, etc.) are generally used to toughen polymer materials, which will reduce the stiffness and strength of the materials. Using inorganic filler to enhance the toughness will decline; The use of nano-particles, due



to its special structure and performance, can significantly improve the strength, rigidity, toughness of the polymer, with reinforcing and toughening.

The particle size, dosage and surface treatment of nano-particles will have a great influence on the properties of the composites when they are filled with nano-particles to strengthen the polymer materials. With the use of nano-level filler, the size of the particles decreases and the surface area of the particles increases, so the contact area between the filler and the matrix increases. Moreover, the surface active centers of the nano-particles are more, which can be closely combined with the matrix and have good compatibility. When subjected to external force, the particles are not easy to break away from the matrix, and because of the interaction of the external force field, many micro-deformation zones are generated in the matrix, which absorb a lot of energy. This determines that it can not only transfer the external stress, but also cause the matrix to yield, consume a lot of impact energy, so as to achieve the effect of toughening and strengthening at the same time. At present, a variety of nano-particles have been used to fill the polymer materials to achieve high performance and functionalization of polymer materials.

The results of filling PVC with nano- CaCO_3 showed that when the content of nano- CaCO_3 was 10%, the tensile strength of the composite was 123% of pure PVC, and the notch impact strength was 313% of pure PVC. This indicated that nano- CaCO_3 exerted a triple effect on the system, including strengthening, toughening and improving the elongation at break.

The results of filling Polypropylene with nano- CaCO_3 showed that nano- CaCO_3 had an obvious inducing effect on crystallization, which increased the crystallinity of PP and reduced the crystal particles, thus improving the impact strength of PP. On the other hand, due to the characteristics of CaCO_3 nano-particles themselves, they were filled into the polymer and have high bonding strength with the polymer interface, thus improving the mechanical properties of the polymer.

With nano- TiO_2 filling high-impact polystyrene (HIPS) waste, It was found that when TiO_2 content was only 1%, HIPS waste could be reused by improving the material's notch impact strength, tensile strength and heat resistance temperature.

PMMA/ SiO_2 nano-composites were prepared by bulk polymerization (in situ dispersion polymerization). It was found that the tensile strength of materials decreased with the addition of SiO_2 , and increased with the increase of SiO_2 content. At the same time, with the increase of SiO_2 content, the breaking elongation of the matrix first increased, and then decreased. The surface-treated SiO_2 particles had a good interface between the surface and the matrix, so that the adhesion force between the particles and the matrix was high. Under certain stress conditions, the hollowing process of a small number of particles would absorb a considerable part of energy and improve the toughness of the matrix. In addition, under the condition of low content of SiO_2 , particles could move easily in the matrix, and its viscous dragging effect also improved the matrix toughness. On the other hand, due to the crosslinking effect of SiO_2 particles in the matrix, the elongation at break would continue to decline.

Nano-particles play an important role in improving the photoelectric properties of polymers to obtain functional polymer matrix composites due to their many optical, magnetic and electrical properties. For example, the addition of silicon-based nano-powders to PVC can greatly improve the disadvantage of PVC's easy absorption of ultraviolet light and degradation. Because of the small size effect of nano-particles' micropores and the characteristics of silicon-based compounds, complete reflection of ultraviolet light can be generated. The magnetic properties of Fe/PE system were studied, and Fe/PE nanocomposites with high magnetic properties were obtained. A thin layer containing TiO_2 or ZnO particles with a thickness of 1 ~ 10nm was made on EVA, which could absorb ultraviolet light and increase the photoresist of the laminated polymer. In addition, the addition of nano-particles could also improve the thermal properties of polymer matrix and enhance the wear resistance.

3. Mechanism of action of nano-particles on the polymer

It can be seen from the above that nanoparticles have a double positive impact on polymer composites, which is manifested in the properties of simultaneously improving tensile strength and impact strength.

In other words, the toughness of the composite can be improved at the same time. The special effects of nano-particles[3] are mainly due to the particle size, surface structure and volume factors.

It is generally believed that the smaller the particle size of the filler, the larger the specific surface area of the particle, and the more physical and chemical defects on the surface. The approximate relationship between the particle radius and the strength of the composite can be expressed as:

$$\tau_{\max} = 35(1 - \frac{2.71}{1 + r^2}) \quad (1)$$

In the formula, r is the radius of the particle; τ_{\max} is the maximum strength a nanocomposite can obtain. In the case of the same filling amount, the smaller the particle size is, the higher the tensile strength of the composite is, indicating that the smaller the particle size is, the higher the strengthening efficiency of the matrix is.

Due to the special surface structure of nano-particles, they play an important role in the composite process, which can be expressed as the bonding work between nano-particles and the matrix. The relationship between the tensile strength of the composite material and the bonding work between the particle matrix is as follows:

$$\sigma_{y,c} = A \exp\left(\frac{-K_{\sigma,c}}{W_a}\right) \quad (2)$$

In the formula, $\sigma_{y,c}$ is the tensile strength of the composites; A is a constant; $K_{\sigma,c}$ is the parameter related to the content and particle size of the fillers; W_a is the bonding work, which is related to the dispersion force, hydrogen bond and polarization force.

In the formula, $K_{\sigma,c}$ increases with the increase of the content of the filling and decreases with the decrease of the particle size. In addition, the finer the particles are, the less obvious the change of $K_{\sigma,c}$ is with the content. The smaller the particle size of the nano-particle, the greater the hydrogen bond and polarization force, and the larger the contribution of the interface factor of the nano-particle to the bonding work W_a , and the higher the tensile strength of the composite material. In other words, a good interface bonding is one of the guarantees for the composite material to have good physical and mechanical properties. At the nanoscale, many of the components of materials that normally cannot be mixed in a molten or liquid state can be alloying, resulting in a range of novel materials.

In fact, the actual strength of the general material is much lower than the theoretical calculation value, this is because the material itself has many defects (micro cracks, etc.), once impacted by external forces, these cracks will expand, its energy converted into the surface energy of new cracks. When the crack exceeds a certain length, the cracking speed is greatly accelerated. Adding nano-particles into the polymer actually plays a role in energy storage. Particle size, morphology, quantity, surface characteristics, particle distribution and polymer molecular structure, composite and molding process have a significant impact on impact strength. There are a large number of defects on the surface of nano-particles, which not only have the function of energy storage, but also have a strong van der Waals force effect between the nano-particles and the polymer molecular chain. Nano-particles are filled into the defects of the polymer, changing the stress concentration phenomenon of the matrix. Therefore, the toughening and enhancing modification mechanism of nano-particles has the following characteristics:

(1) inorganic nano-particles in polymer matrix, as the crosslinking point of polymer molecular chain, contribute to the tensile strength of the composite;

(2) inorganic nano-particles have the balance effect of stress concentration radiation. By absorbing shock energy and radiation energy, the matrix has no obvious stress concentration phenomenon and reaches the mechanical balance state of composite materials;

(3) inorganic nano-particles generate the energy transfer effect, which can suffocate and passivate the matrix resin crack growth. As cracks are finally terminated, destructive cracking can be avoided;

(4) as the particle size decreases, the specific surface area of the particle increases, and the contact area between the nano-particle and the matrix increases. When the material is impacted, more micro-cracks are generated and more impact energy is absorbed;

(5) if the amount of nano-particles is too much or the particle size of the filler is large, the stress concentration of the composite material is relatively obvious, and the micro crack is easy to develop into macro crack, resulting in the decline of composite material performance.

4. Influencing factors of dispersion effect of nano-particles

The uniform dispersion of inorganic nano-particles in polymer matrix is the key to prepare polymer/inorganic nano-particle composites with excellent properties. Therefore, it is very important to study the dispersion mechanism of nano-particles in polymer matrix. However, there are few reports on this aspect. At present, there are two main methods to improve the dispersion of nano-particles in polymer matrix: one is surface treatment of nano-particles; the second is to improve the mixing effect in the process of dispersion.

4.1 Influence of surface treating agent on dispersion effect

Nano-particle dispersion is the process of separating the aggregates of nano-particles into individual nano-particles or small aggregates of a few nano-particles uniformly distributed in the polymer. Therefore, in the preparation of polymer nanocomposites, the agglomeration of nano-particles should be modified by surface treatment. The surface treatment agent is used to cover the particle surface and endow the particle surface with new properties, which can prevent the group polymerization and promote its softness with the polymer and dispersion in the polymer. The surface modifiers commonly used are silane, titanate coupling agent, stearic acid, organic silicon, etc. At present, macromolecular coupling agent also has a great development, because macromolecular coupling agent has amphiphilic structure, and its oil-wet chain end length is longer than the common coupling agent, and the compatibility with polyolefin resin is better. For example, the graft copolymerization of PE with maleic anhydride can connect the polar groups to the PE molecular chain and serve as macromolecular coupling agent on the composite material to coat the filler surface.

Wang xu et al.[4] studied the dispersion law of nano- CaCO_3 in PS, they found that using ordinary mixing equipment to surface treatment of nano- CaCO_3 could not provide enough dispersion force to completely disperse the agglomerated nano- CaCO_3 and the coupling agent could not completely permeate the particles and cover the surface of the particles, the additional coupling agent was very unfavorable to the dispersion of nano- CaCO_3 , it would have the effect of lubricant, affecting the broken energy transfer between PS melts and particles; it also clinged around the particle aggregates and acted as a "shell". At the same time, this part of coupling agent also acted as the bridge force of the liquid, further increasing the agglomeration force between particles, which seriously hindered the dispersion of nano- CaCO_3 particles in PS. Therefore, if the surface of the nano-particles was not properly treated, the dispersion effect in the polymer was worse than that of the untreated nano-particles. They also found that the dispersion effect of the tensile flow was better than that of the shear flow. For the same material, increasing the shear rate (tensile rate) was beneficial to improve the dispersion effect.

Wu lei et al.[5] used titanate coupling agent for surface grafting modification of nano- CaCO_3 , melt-mixing process was used to prepare polypropylene (PP) / ethylene-octene block copolymer (OBC) / nano- CaCO_3 composites. The effects of nano- CaCO_3 adding amount on mechanical, thermal and rheological properties of the obtained composites were investigated, as well as the fractured surface morphologies. The results showed that when the adding amount of modified nano- CaCO_3 reached 2.5%, the maximum values of mechanical properties of the obtained composites appeared (tensile strength :27.5 MPa, impact strength:16.1 kJ / m^2). The serious aggregation effect of nano-particles led to a sharp degradation in mechanical properties with further increasing the adding amount of nano- CaCO_3 . Nano- CaCO_3 served as an effect of heterogeneous nucleating agent ,

increasing the crystallization temperature and crystallinity of the obtained composites. Furthermore, the complex viscosity and storage modulus of the obtained composites had shown an increase as a result of the presence of nano-particles.

4.2 Influence of processing machinery and process on dispersion effect

It is difficult to achieve nano-level dispersion of nano-particles in the polymer by using the traditional blending method. At present, the main equipment and processing methods can be used are: 1) wet grinding method 2) high-speed mixing 3) ultrasonic vibration treatment 4) vibration mill 5) adding effective mixing device 6) large length-diameter ratio screw rod, and so on.

Qu Jinping[6] from south China university of technology used electromagnetic dynamic injection molding machine to induce injection molding of polypropylene (PP) –nano-CaCO₃ composite material with pulsating pressure. By increasing the amplitude and vibration frequency in processing engineering, nano-CaCO₃ was dispersed more evenly in PP melt, and the tensile strength and impact strength of pp-nano-CaCO₃ composite material were improved compared with the steady-state (no vibration was applied).

Ultrasonic wave dispersion utilizes local high temperature, high pressure or strong shock wave and micro-jet generated during ultrasonic cavitation to weaken the nano-action energy between nano-particles and effectively prevent the agglomeration of nano-particles. Li Xiaobing et al.[7] prepared epoxy resin (EP)/nano-SiO₂ composite material by ultrasonic wave, and found that ultrasonic wave could significantly promote the dispersion of nano-SiO₂ in EP. Wang Xu et al.[8] prepared Polystyrene / nano-CaCO₃ composite by directly acted ultrasonic wave on the melted granule prepared by twin-screw extruder. TEM observation showed that ultrasonic wave could significantly improve the dispersion degree of nano-CaCO₃ in PS matrix. Ultrasonic treatment of PP/ nano-CaCO₃ composite with high filling amount not only promoted the dispersion of nano-CaCO₃ in PP, but also made nano-CaCO₃ into a chain-like distribution in the matrix which increased the flexural modulus of PP composite by 44%. However, it was still possible to reunite the nano-particles if the ultrasonic oscillation stopped. In addition, the dispersion effect of ultrasonic wave on extremely small nano-particles was not ideal, because when the ultrasonic wave was dispersed, the resonance of the particles accelerated and the collision energy of the particles increased, which could lead to agglomeration.

5. Conclusion

Research and development of nanocomposites have revolutionized the way materials and products are produced and the range of properties that can be achieved. The uniform dispersion of inorganic nano-particles in polymer matrix is the key to prepare polymer/inorganic nanocomposites with excellent properties. Therefore, the dispersion mechanism of nano-particles in the polymer matrix needs to be studied in depth to obtain high-performance polymer nanocomposites, so that the composite materials can be designed on the nanoscale. The solution of the above problems in the future will be of great significance to promote the further industrial application of polymer/inorganic nanocomposites.

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