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Nanometre-sized TiO_2 as applied to the modification of unsaturated polyester resin

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Abstract

Nano-materials can be used as filler for polymers. Thereby, the mechanical properties of the obtained materials can be obviously improved. In this paper, nanometre-sized TiO_2 was used as filler for unsaturated polyester (UP) resin, and the effect of the amount of the filler on the mechanical properties of this material was discussed.

Keywords: Nano-TiO_2; Filling modification; Unsaturated polyester resin

1. Introduction

With the development of the technique of inorganic particles microdispersion and the technique of surface treatment of particles, the toughening modification of plastics has changed the used method of filling elastic bodies such as rubber, which can damage the rigidity, the stability in size and the heat resistance of the modified materials.

For composite materials, rigid inorganic particles can also withstand tensile stress and further toughen and strengthen the resin matrix if they have an excellent binding effect in the matrix. Thus composite materials with excellent properties are obtained [1]. When nanoparticles are filled in polymers, the rigidity, the stability in size, and the thermal stability of the particles can benefit the toughness, the processability, and the electric inductivity of the polymers.

In this study, nanometre-sized TiO_2 was used as the filler, unsaturated polyester (UP) resin as the polymer matrix, and TiO_2/UP nano-composite materials were prepared by mixing them carefully.

2. Experimental

TiO_2 with the size of 27 nm was prepared in our laboratory. UP, type S-583 for general utility, was provided by the General Factory of Composite Materials in Nanjing. Petroleum ether (analytical purity) was provided by Shuanghuan Chemical Test Solvent Factory in Beijing. Peroxymethylethylketone (initiator) and cobalt octylicate (accelerator) were purchased from the General Factory of Composite Materials in Nanjing.

A KQ-250-type ultrasonic wave washing machine was used to disperse the nanoparticles homogeneously. The tensile and bending strengths were tested by an AGS mechanical property test machine. The tensile rate was 50 and 20 mm min^{-1}, respectively. The measurements were carried out at 15 °C. The impact property was tested via a pendulum impact test machine.

A certain amount of UP was evacuated to get rid of the air in it and a certain amount of nanometre-sized TiO_2, which had been calcinated at 300 °C for several hours, was mixed with the resin. The mixture was stirred to be homogeneous. Then some accelerator was added in the mixture, and some amount of initiator was added successively during stirring. The mixture was homogenized with the help of an ultrasonic treatment, and finally poured and cured in a mould at room temperature. The amounts of the filler were 2, 3, 4, 6 and 9 wt.% of UP.

The effect of ultrasonic vibration was as follows: The diameter of a nanoparticle is small (1 nm), the specific surface area is large, and the surface energy is high. Thus the adhesive force between the nanoparticles is strong and the particles easily agglomerate. Relatively large agglomerating bodies with a number of weak joining interfaces are thus formed. The ultrasonic wave can break the agglomerating bodies and make them disperse in the liquid medium. The mechanism is that the ultrasonic vibration can damage the Coulomb and van der Waals forces between the particles and make them homogeneously dispersed in the medium.

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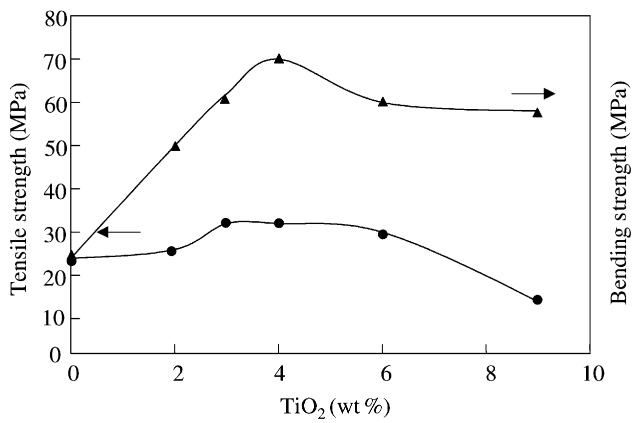

Fig. 1. Relationship between the amount of TiO_2 and the tensile and bending strengths of UP.

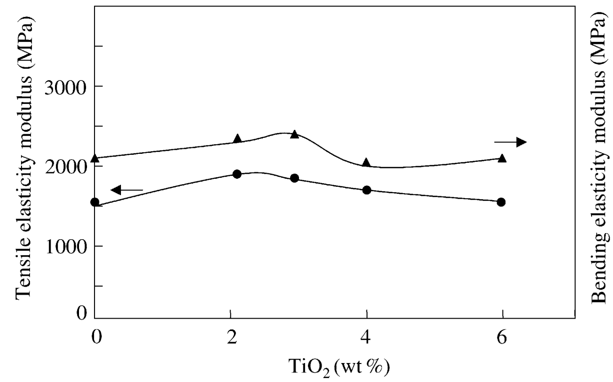

Fig. 2. Relationship between the amount of TiO_2 and the tensile and bending elasticity moduli of UP.

3. Results and discussion

The amount of nanometre-sized TiO_2 has influence on the tensile and bending strengths of UP (Fig. 1). The two curves go up as the filling amount increases. The two strengths reach the maximum when the filling amount is 4 wt.%, and then the curves go down as the filling amount is more than 4 wt.%. At maximum, the tensile strength increases by 47% and the bending strength by 173%. It is demonstrated that TiO_2 has a reinforcement effect on UP and the optimum filling amount is 4 wt.%.

According to Griffith's theory [2], the strength of materials can be expressed as follows:

$$\sigma = A\left(\frac{E\gamma}{C}\right)^{1/2} \tag{1}$$

where E is the elasticity modulus, γ the effective surface energy, C the effective defect size, and A the ratio factor. From the formation process of apertures, it is known that the defect size depends on the size of the filling particles approximately. The finer the particles, the smaller the defect size and the higher the strength. So nanometre-sized TiO_2 is very useful to improve the strength of materials. The size of the nanoparticles is small and their specific surface areas are large. There are so many physical and chemical defects on the surface that the particles have a lot of physical and chemical binding opportunities with the polymer chains. So the adhesive forces between the fillers and the matrix are strong, and thus the strength of the resin matrix is improved. But the small size of the particles causes agglomeration easily. As the particle concentration increases, the agglomeration of the particles takes place. The particles are difficult to disperse and the strength of the resin matrix decreases.

Another explanation [3] is that when the filling amount is small, the particles disperse homogeneously in the composite. The authentic strength of the composite depends on the strength of the interfaces. The atomic position gradient between the particles is small and the elasticity scale is wide, so that the allowed shift of the atomic elasticity is wide and that leads to an improvement of the tensile strength of the material. As the filling concentration increases continuously, the expansion of microfine phase change occurs which leads to an enlargement of the particle diameter, thereby decreasing the tensile strength.

Fig. 2 shows the relationship between the amount of TiO_2 and the tensile and the bending elasticity moduli. At the beginning, as the amount of the filler increases, the elasticity moduli increases continuously. When the amount is 3–4 wt.%, the two moduli have a maximum, and then they decrease as the amount of TiO_2 increases. At maximum, the tensile and bending elasticity moduli improve by 22 and 12%, respectively. It is concluded that nanometre-sized TiO_2 particles improve the elasticity modulus of UP.

The elasticity modulus is one of the important parameters characterizing the rigidity of a material. The mechanical properties of the composite are decided to a great extent with the composition and the shape of the interfaces between the filler and the matrix, and they also have relations with the diameter, the content, and the dispersion of the filler in the matrix. According to Shang's explanation [4], nanoparticles can adsorb and bond with polymers sufficiently and thus improve the rigidity of the matrix.

Nanometre-sized TiO_2 is a kind of high-elasticity modulus material. According to the elasticity modulus equation of the filled composite which is expressed below, it is determined that there is at least one E_f value which is much more than the E_p value. So the elasticity modulus of the composite is higher than that of the resin matrix.

$$E_c \geq \frac{E_p E_f}{E_p V_f + E_f V_p} \tag{2}$$

where E_c, E_p and E_f are the elasticity moduli of the composite, the resin matrix and the filler, respectively, and V_p and V_f are the volume percentages of the resin matrix and the filler, respectively.

Fig. 3 shows the relationship between the amount of TiO_2 and the impact strength and the elongation at break. As the amount of TiO_2 increases both the impact strength and the

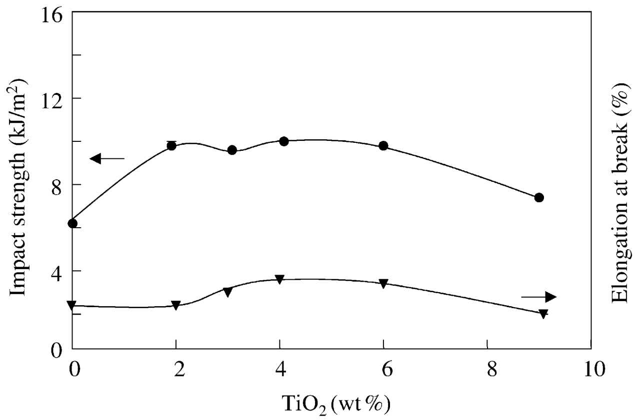

Fig. 3. Relationship between the amount of TiO_2 and the impact strength and elongation at break of UP.

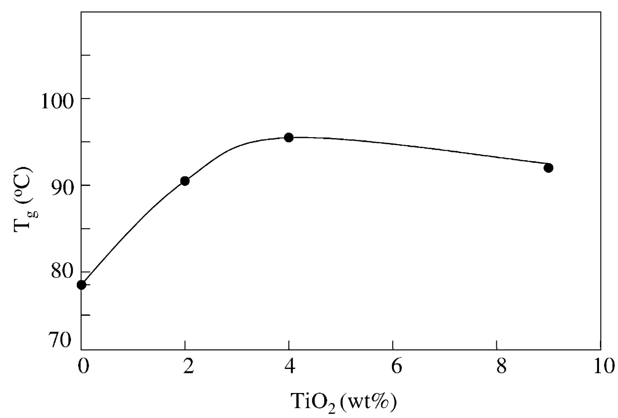

Fig. 4. Influence of the amount of TiO_2 on the glass transition temperature.

elongation at break increase continuously, reach a maximum when the amount of TiO_2 is 4 wt.%, and then they decrease. At maximum, the impact strength improves by 60% and the elongation at break by 48%.

A general explanation [1] of the toughening modification mechanism of nanoparticles can be concluded as follows:

1. Rigid inorganic particles produce a stress concentration effect. The effect initiates the surrounding resin to produce microgaps which absorb some deformation work.
2. Rigid inorganic particles prevent and inactivate the development of fissures in the resin matrix.
3. The specific surface area of nanoparticles is large, and this leads to a large contact area between the filler and the matrix. When materials are impacted they can produce more microgaps and absorb more impact work. But if the amount of the filler is excessive (>4 wt.%), the particles are so close to each other that the microgaps easily develop to macrogaps, and the properties decrease.

In order to give a further explanation of the strengthening and toughening mechanisms of the composite, we determined the compatibility between the TiO_2 nanoparticles and the UP on the basis of the glass transition temperature (T_g) tested with differential scanning calorimetry (DSC). On the basis of the above DSC results (Fig. 4), the mechanical properties of the TiO_2 modified UP were analyzed. Two conclusions can be drawn: (1) The T_g value of UP can be improved when TiO_2 is added. (2) T_g increases up to a maximum and then decreases as the amount of TiO_2 increases. At maximum, the amount of TiO_2 is 4 wt.%.

It is known [5] that the compatibility between different substances can be characterized with T_g. If the TiO_2 nanoparticles have a good compatibility with the UP, the T_g value of the composite is much higher than that of the UP. The better the compatibility, the higher the T_g value of the composite. The T_g value of nanometre-sized TiO_2 is equal to its melting point, i.e., its T_g value is very high and does not appear in the temperature scale of DSC. So a TiO_2/UP composite has only one T_g value. The DSC analysis corresponds well to the former experimental results.

4. Conclusions

1. The mechanical properties of UP can be improved when nanometre-sized TiO_2 is added. When the amount of TiO_2 is 4 wt.%, the tensile strength improves by 47%, the bending strength by 173%, the tensile elasticity modulus by 22%, the bending elasticity modulus by 12%, the impact strength by 60%, and the elongation at break by 48%.
2. From the DSC analysis it is concluded that nanometre-sized TiO_2 has an excellent interface adhesion with the UP matrix. When the amount of TiO_2 is 4 wt.%, it has the best compatibility with the UP matrix.

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