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Modification of mechanical properties by TiO_2 nano-particle for biodegradable materials made from palm oil sludge and activated sludge cake

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Abstract: Titanium dioxide (TiO_2) nano-particle is widely used in composite materials to its improved mechanical properties. TiO_2 nano-particle was used in the composite material that consists of palm oil sludge from the palm oil production and activated sludge cake from a papermaking process. TiO_2 was synthesized by a hydrolysis of titanium isopropoxide. The parameter was investigated by the mole ratio of reactant to different solvents (isopropanol and isobutanol). The solution was prepared by adjusting pH to acid solution, resulting in different sizes and distributions of precipitate which was heated at different temperatures. The obtained samples were then morphologically and structurally characterized using X-ray diffraction (XRD) and particle size distribution (PSD). The experimental results show that the TiO_2 sample from isopropanol solvent with heated temperature of 600 °C exhibits the best results. Consequently, different mass fractions of TiO_2 (0, 0.5%, 1.0%, 2.0%, 4.0% and 8.0%) were used for specimens that were made from palm oil sludge mixed with activated sludge cake. All samples were later characterized by 3-point bending test and compression test. The results indicate that the adding 0.5% and 1.0% TiO_2 particles to the composite material outperforms the other fractions in terms of enhancing mechanical properties. Nonetheless, mechanical properties tends to decrease when adding 2.0% TiO_2.

Key words: titanium dioxide; palm oil sludge; active sludge cake; composite; mechanical properties

1 Introduction

The growing production and mass-volume use of petroleum plastics and composites in everyday life has led the accumulation of tremendous amount of non-degradable wastes, which have become a serious and urgent threat to the environment [1]. Therefore, environmental friendly materials has been chosen. Composite materials are focused because they usually have higher mechanical properties and longer lifetime than other materials. Composite materials are engineered or naturally occurring materials that are made from two or more constituent materials with significant difference in physical or chemical properties. Those properties remain separated and distinctive at the macroscopic or microscopic scale within the finished structure [2]. Recycling process utilizes old or waste materials to produce new products. Examples of recycled products can be composite materials from waste product [1,3−5] and biodegradable adhesive [6−8]. One main purpose of utilizing waste materials in recycling process is to prevent potential wastes to be worthlessly discarded and to reduce the consumption of fresh raw materials as well as to alleviate the environmental problems arisen from polluted resources and landfills.

Titanium dioxide (TiO_2) nano-particle is widely used as filler agent to improve mechanical properties of composite materials. TiO_2 is the naturally occurring oxide of titanium and has a form of crystal structure of anatase, rutile, or brookite. Presently, TiO_2 has been extensively studied for various electronic applications. Its photocatalytic nature and transparent conductivity are strongly dependent upon the crystalline structure, morphology and crystallite size. Due to the photo-semiconductor properties of TiO_2, one may find its applications as antibacterial agent for the decomposition of organisms. TiO_2 of the anatase crystalline form is a strong bactericidal agent when exposed to near-UV light [9].

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The preparation condition of the nanometer TiO_2 powder was attempted to optimize by different solvents and calcination temperatures. With an evaluation on compressive strength, an optimal fraction of TiO_2 nanoparticle for the composite material that made from palm oil sludge mixed with activated sludge cake was investigated, and tapioca starch was used as biodegradable adhesive.

2 Experimental

2.1 Synthesis of TiO_2 nanopaticles

The initial solution was a mixture of 5 mL titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) and two kinds of solvents (isopropanal and isobutanal) with the mole ratio between reactant to solvent was 1:30. The volume was adjusted to 250 mL with distilled water. The pH value of solution was adjusted to pH=2 by adding HNO_3 or NH_4OH. Hydrolysis of the turbid solution was heated up to 70 °C in water bath for 18−20 h. After process, the solution was dried into a crystalline white solid. The prepared precipitates were washed with ethanol and dried for several hours at 100 °C. They were dried again in a vacuum system for 3 h to obtain a yellow-white powder. The prepared powder was calcined at varied temperature of 600 °C and 800 °C for 2 h [10]. The obtained samples were then structurally characterized by means of X-ray diffraction (Bruker D8 ADVANCE), which was used to identify the crystal phase and estimate the average crystallite size as well.

2.2 Preparation of specimens

The composite material specimens made from palm oil sludge were mixed with activated sludge cake. Both materials were sifted with a sieve sized 500 μm and a mixing ratio between palm oil sludge to activated sludge cake was 3:1. The biodegradable adhesive was prepared by 10% tapioca starch. Six different types of specimens were prepared based on different mass fractions of TiO_2 (anatase phase) at 0, 0.5%, 1.0%, 2.0%, 4.0% and 8.0% (mass fraction). The compression machine was used to fabricate the specimens. Length, width and dept of each specimen are 90 mm, 25.4 mm and 3 mm, respectively. Later, the specimens were characterized by 3-point bending test and compression test.

2.3 Flexural properties

Flexural properties of the specimens were obtained by three-point bending test according to ASTM D-790. The testing was carried out at room temperature (23±1) °C) by Instron machine No.5530 at crosshead rate of 3.0 mm/min. Flexural stress and strain were measured in three-point bending using specimen with cross-sectioned dimensions 3 mm×25.4 mm and 90 mm in length. The length between support span was 40 mm as recommended by the standard.

2.4 Compression resistance

Compression resistance of the specimens was carried out using Testometric Universal Machine No. 2696 at crosshead rate of 30 mm/min and room temperature of (23±1) °C. Each specimen was tested according to ASTM D 642. The values of load at peak and load at break were measured.

3 Results and discussion

3.1 Analysis of TiO_2 nanopaticles

The preparation of the TiO_2 colloids in the nanometer range can be effectively conducted through the hydrolysis and condensation of titanium alkoxides in aqueous media. Alkoxides are hydrolyzed and subsequently polymerized to form, in the presence of water, a three-dimensional oxide network. The reactions can be systematically represented as

$$Ti(OR)_4+4H_2O \longrightarrow Ti(OH)_4+4ROH \tag{1}$$

$$Ti(OH)_4 \longrightarrow TiO_2{\cdot}xH_2O+(2-x)H_2O \tag{2}$$

where R is ethyl, *i*-propyl, *n*-butyl, etc [11]. It is common to know that the tetravalent cations are so acidic that the nucleation of stable hydroxide $Ti(OH)_4$ cannot occur.

Water molecules formed according to reaction (2) always bear a positive partial charge [12]. Therefore, oxolation and olation proceed simultaneously during nucleation and growth, leading to the formation of amorphous hydrous oxide ($TiO_2{\cdot}nH_2O$). The precipitation of TiO_2 leads to rutile or anatase phases [13]. Such structures from aqueous molecular precursors are formed. Non-occurrence of deoxolation ($O{=}Ti - OH_2 \longrightarrow HO{-}Ti{-}Ti{-}OH$) during nucleation olation leads to a linear growth along one of the two equivalent directions in the equatorial plane of $[Ti_2O_2(OH)_4(OH_2)_4]^0$ dimers. Oxolation between the resulting $TiO(OH)_2(OH)_2$ linear chains after an internal proton transfer leads to corner-sharing octahedral chains (Ti_3O bridges) characteristics of the rutile structure. The formation of rutile may be associated to the metastability of apical $Ti{=}O$ bonds within monomers or dimers. If deoxolation occurs prior to olation, condensation can proceed along apical direction, leading to skewed chains typical of the anatase structure. Controlling the stage of deoxolation prior to olation is obtained just by adjusting the pH and initial water concentration. This control leads to precipitation of anatase nanopowder TiO_2 in the experimental procedure [10].

Figure 1 shows the XRD pattern of the prepared powder in different solvents at the different calcinations temperature. The plane diffraction peak is used for anatase and rutile. It shows that the volume of anatase phase in isopropanol solvent is more than isobutanol solvent. The volume of anatase phase decreases when the calcination temperature was up to 800 °C. This temperature has been mostly reported from 600 to 900 °C for the initiation and finishing temperature respectively [14].

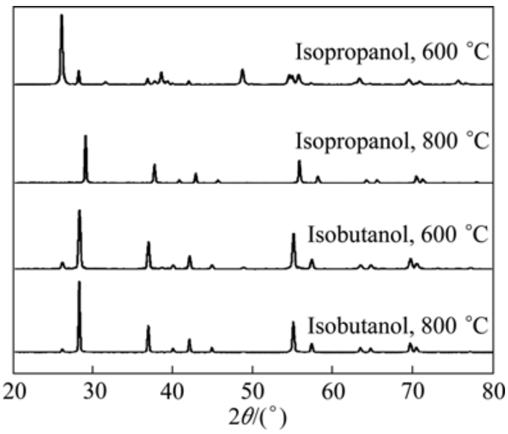

Fig. 1 XRD patterns of TiO_2 particles obtained from different solvents and temperatures

It is then possible to assume that the growth of rutile particle starts right after its nucleation. In fact, this reveals that nucleation and growth of rutile phase would have been initiated at temperature somewhere from 400 to 600 °C [10,15].

3.2 Mechanical properties of composite material

The fabricated composite material specimens made from palm oil sludge mixed with activated sludge cake by compression method is shown in Fig. 2. According to the results of mechanical properties, a comparison of the flexure stress at maximum flexure strain and maximum flexure stress of 3-point bending of the five samples were compared as shown in Fig. 3. According to the results, it is found that the flexure stresses at maximum flexure strain has similar values, but the maximum flexure stress increases by the addition of TiO_2 nanopaticles. In the case of 0.5% and 1.0% TiO_2, the maximum flexure stresses remarkably increase. However, the maximum flexure stress is not improved as the addition amount of the TiO_2 nanoparticles increase. It is obviously seen that the flexural stress tends to decrease when TiO_2 is over 2.0%. Figures. 4 and 5 show the maximum flexure load and elastic modulus, respectively. The results are consistent with maximum flexure stress, remarkable increase by the addition of 0.5% and 1.0% TiO_2, with the highest at the 1.0% TiO_2. However, the elastic modulus decreases when the addition of TiO_2 is over 2.0%.

Fig. 2 Specimen made from palm oil sludge mixed with activated sludge cake by compression method

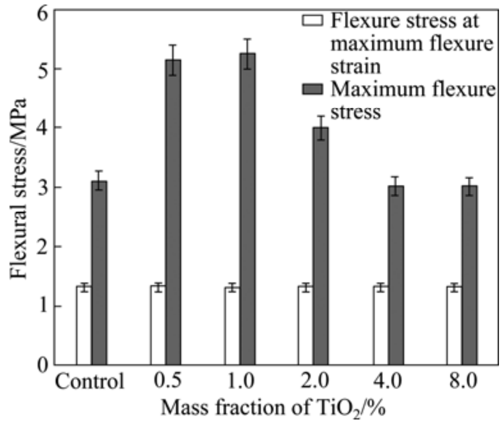

Fig. 3 Comparison of flexure stress at maximum flexure strain and maximum flexure stress of 3-point bending

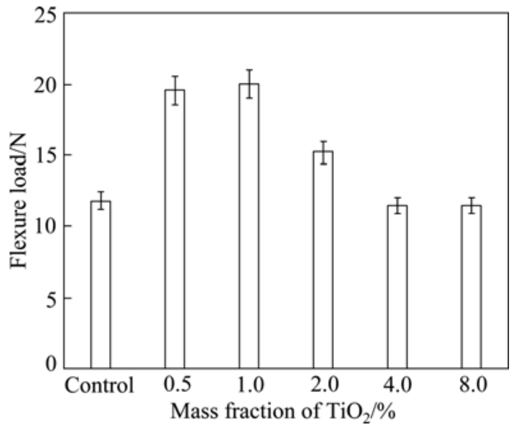

Fig. 4 Maximum flexure load of composites at different mass fractions of TiO_2

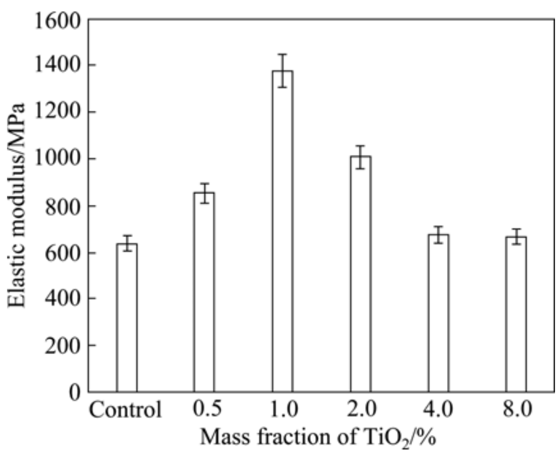

Fig. 5 Elastic modulus of composites at different mass fractions of TiO_2

In general, there is a strong argument in the aforementioned literature over the effect of filler content researcher results show that the flexural strength of on the flexural strength of modified composite. Some microparticle-filled composites is reduced with rising filler content [16], while others argue that flexural strength increases with nano particles [17].

Figure 6 shows a comparison of the load at peak and load at break of compression test. Based on the results, the values of load at peak are more than the values of load at break. Both values tend to remarkably increase by adding 0.5% TiO_2 nanoparticles. However, the values decrease with the mass fraction of TiO_2 increasing.

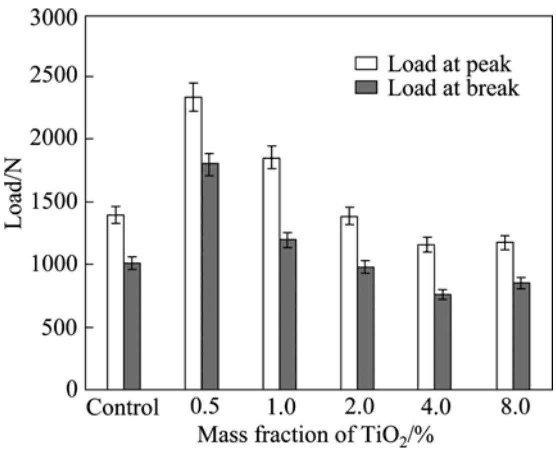

Fig. 6 Mass fraction vs load at peak and break of compression test at different mass fractions of TiO_2

In order to explain this phenomenon, the following should be considered. The dispersion state of the nanoparticles and the interface in composites occur. Regarding the first factor, the agglomeration is likely to be formed more at higher filler content, and that may cause embrittling effects. Large agglomerates in the matrix cause a propagation crack and induce the initiation of the final failure [18].

As discussed earlier, the nano-particles interface in composites plays a major role in the improvement of mechanical properties. Stresses transfer and elastic deformation from the matrix to the fillers are governed by the interface quality [19]. The nano-particles with 1% TiO_2 are able to induce further mechanisms of failure without blocking matrix deformation. According to the crack pining theory, particles may act as obstacles to crack growth by pinning [20]. When fillers exceed 1% (mass fraction), a large number of fillers dominate and reduce the matrix deformation. This indicates that there is not increasing significantly when the filler content is above 1%.

4 Conclusions

Nanocrystalline TiO_2 powder were prepared by the hydrolysis of titanium isopropoxide alcoholic solution. Rutile phase is formed at calcinations temperatures 600 °C and grew slightly when heated up to 800 °C. Mechanical properties of the composite material specimens made from palm oil sludge mixed with activated sludge cake, tapioca starch as biodegradable adhesive and TiO_2 nanoparticle remarkably increase as the addition proportion of TiO_2 nanoparticle increases. However, the additional amount of TiO_2 nanoparticles could cause the depletion in mechanical properties. Therefore, it can be concluded that adding 0.5% TiO_2 particles can be an optimal proportion for the composite material since it outperforms the other fractions in terms of enhancing mechanical properties.

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