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Homogeneous nanoparticle dispersion prepared with impurity-free dispersant by the ball mill technique

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ABSTRACT

The homogeneous dispersion of nanoparticles in solvents or polymer matrices is essential for practical application of nanocomposites. In this study, the planetary ball milling technique was used to de-agglomerate silica nanoparticles in butyl acetate. The size of the nanosilica aggregates was evaluated by TEM and SEM. With the addition of polyacrylate polymer to the organic solvent, the nanoparticle agglomerates were effectively broken up by planetary ball milling at the proper milling time; however, re-agglomeration occurred after a longer milling time. The results of TGA and FTIR indicated that the polyacrylate molecules could be adsorbed *in situ* onto the nanoparticles. Behaving similar to a dispersant, the adsorbed polyacrylate reduced the blend viscosity significantly and prevented re-agglomeration of the nanoparticles. Utilizing the polyacrylate polymer both as the dispersant and the polymer matrix, the polyacrylate-based nanocoatings were further prepared. The optical transmittance and haze value of the nanocoatings were found to be sensitive to the dispersion level of the nanoparticles, and the elastic modulus and hardness of the nanocoatings were improved in comparison with those of the neat polymer coating.

1. Introduction

Nanocomposites have attracted considerable research interest in the past few years. Incorporation of inorganic nanofillers into polymer matrices has been effective for the improvement of various properties of the matrices, such as the creep resistance (Zhang, Yang, & Friedrich, 2004), the wear and friction resistance (Ma, Zheng, Cao, & Guo, 2010; Malzbender & de With, 2001; Zhang, Tang, Zhou, Eger, & Zhang, 2011), the thermal, electrical and mechanical properties (He, Zhang, Li, Fang, & Shi, 2011; Jia et al., 2012; Li et al., 2011) and so on. As a branch of the nanocomposite field, the research and applications of transparent nanoparticle-reinforced coatings have gradually increased in recent years. The addition of nanoparticles to polymers causes a significant increase in their anti-scratch ability; therefore, the nanocoatings can be used as anti-scratch protective coatings for conventional transparent plastics poly(methyl methacrylate) (PMMA), polycarbonates (PC), poly(ethylene terephthalate) (PET) (Zhang et al., 2010). It is well established that the homogeneous distribution of nanoparticles in polymer coatings is critical because larger nanoparticle aggregates can interfere with light and disrupt the optical properties of the coatings (Naganuma & Kagawa, 2002). Although aggregate-free nanoparticle dispersions have often been prepared via sol–gel techniques, the most frequently used method in industry to prepare nanoparticle dispersions is still mechanical mixing, such as high-speed shear milling, three-roll milling, and high-pressure homogenizing, among others. Considerable efforts have been made to obtain homogeneous and stable nanoparticle dispersions by mechanical mixing, as reported in the literature (Müller, Peukert, Polke, & Stenger, 2004).

When nanoparticles are mixed with solvents using mechanical mixing, various dispersants must be added to prevent the agglomeration and precipitation of nanoparticles as a result of electrostatic, steric, and electrosteric stabilization effects (Iijima, Kobayakawa, Yamazaki, Ohta, & Kamiya, 2009; Reindl et al., 2008). However, if the dispersants are not compatible with the polymer matrices, they will cause re-agglomeration of the nanoparticles when the nanoparticle dispersions are further mixed with the polymer resins. In addition, the dispersant may act as an "impurity" in the resulting composite material and may impart negative effects on the material. For example, inappropriate dispersants will degrade the insulating properties of silicone-based coatings. From the above discussion, it can be concluded that the ideal dispersant would be the polymer matrix itself as these problems could

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be avoided. However, to the best of our knowledge, only a few studies have been reported in which the polymer matrix functions as the dispersant. For example, Lin et al. (2003) modified single- and multi-walled carbon nanotubes using poly(vinyl alcohol) (PVA) as the dispersant through esterification reactions and then compounded the modified carbon nanotubes with the PVA matrix.

In this work, nanosilica particles were mechanically mixed with an organic solvent (butyl acetate) using planetary ball milling, which is a simple and efficient technique for dispersing nanoparticles as a result of the high impact and friction forces generated in milling process (Avettand-Fènoël, Taillard, Dhers, & Foct, 2003; Hedayati, Salehi, Bagheri, Panjepour, & Maghzian, 2011; Kollo et al., 2010; Oliveira, Chen, & Ferreira, 2002). The polyacrylate polymer was used both as the dispersant and the polymer matrix. A homogeneous nanosilica dispersion was obtained in the presence of a polyacrylate polymer. The nanocoatings were also prepared and characterized.

2. Experimental

2.1. Materials

Pyrogenic silica nanoparticles (R9200) with a primary particle size of 13 nm were kindly supplied by Evonik Industries AG (Germany). According to the datasheet supplied by Evonik Industries AG, these pyrogenic silica nanoparticles contain a certain amount of methyl groups on their surface. Polyacrylate and the curing agent aliphatic polyisocyanate were obtained from the Huayuan Painting Co., Ltd., Changzhou, China. Butyl acetate (≥99%) and ethanol (≥99%) were purchased from the Sinopharm Chemical Reagent Beijing Co., Ltd., (Beijing, China). All materials were used as received without further purification.

2.2. Mechanical dispersion of pyrogenic nanoparticles

Butyl acetate and silica nanoparticles (30 wt.%) were mixed using a magnetic stirrer; the suspension was then processed using a laboratory planetary ball mill (PM100, Retsch GmbH, Haan, Germany). Yttrium–stabilized ZrO_2 balls with a uniform diameter of 2 mm were utilized as the milling media. In some cases, the polyacrylate resin was added to the suspension to act as the dispersant. The dispersant-to-nanoparticle weight ratio and the ball-to-nanoparticle weight ratio were determined by trial-and-error, and the values were set to 0.67:1 and 10:1, respectively. The rotation speed of the grinding vial was set at 500 rpm. To avoid excessive heating of the milled dispersion and equipment, the operation cycle of the milling process was set as follows: every 5 min of active milling was followed by 2 min of rest. Milling times from 2 to 24 h were utilized. The main parameters for the planetary ball milling process are shown in Table 1.

Table 1
Main parameters of planetary ball milling process.

Parameter	Value
Effective radius of disc wheel (mm)	245
Disc speed of rotation (rpm)	500
Vial-to-disc speed ratio	−2:1
Material of grinding vial	Yttrium stabilized ZrO_2
Volume of grinding vial (mL)	125
Radius of grinding vial (mm)	61
Material of milling balls	Yttrium stabilized ZrO_2
Ball diameter (mm)	2
Ball-to-powder ratio	10
Milling time (h)	0, 2, 6, 12, 24

2.3. Coating preparation

The dispersion containing 30 wt.% of silica nanoparticles was diluted with the polyacrylate resin to a filler content of 10 wt.%. After addition of the curing agent (polyisocyanate), the solution was further stirred at 500 rpm for 12 h. Finally, the solution was spin-coated onto PMMA substrate and cured at 65 °C for 12 h. The thickness of the coatings can be controlled at ~20 μm.

2.4. Characterization

The rheological behaviors of the nanoparticle dispersions were characterized by a HAKKE MARS2 rheometer (Thermo Scientific, Waltham, MA, USA) at 25 °C in the cone and plate configurations (plate diameter = 35 mm, cone angle = 1°). The shear rate was increased from 0 to 100 s^{-1} over 3 min.

To verify if any interactions exist between the nanoparticles and the polyacrylate resin during the milling process, the nanoparticle dispersion was diluted with excess ethanol, sonicated for 20 min and then centrifuged at 5000 rpm for 20 min. The obtained precipitate (a white powder) was washed three times according to the above procedure. Finally, the precipitate was dried at 80 °C under reduced pressure overnight before further characterization. The precipitate was analyzed by Diamond TG/DTA (Perkin–Elmer Instruments, Waltham, MA, USA) with a heating rate of 10 °C/min from room temperature to 800 °C under a nitrogen atmosphere. The chemical structures of the precipitate, the unmodified nanoparticles and the polyacrylate resin were also analyzed by Fourier transform infrared (FTIR) spectroscopy (Spectrum One, Perkin–Elmer Instruments, Waltham, MA, USA) in the wavenumber range from 400 to 4000 cm^{-1} with a resolution of 1 cm^{-1}.

A drop of 0.5 wt.% dispersion of silica nanoparticles was cast onto a carbon-coated copper grid and dried at room temperature. The dispersion level and morphology of the nanoparticles were observed using a transmission electron microscope (TEM, Tecnai 20, FEI, Hillsboro, OR, USA) at an accelerating voltage of 120 kV. The fracture surfaces of the nanocoating samples that were frozen and broken in liquid nitrogen were gold-sputtered and observed using a scanning electron microscope (SEM, S-4800, Hitachi Co., Tokyo, Japan). The average particle size of the nanosilica was further obtained from the SEM micrographs using image analyzer software (Nano Measurer 1.2). For each sample, 6 SEM micrographs and a total of 180 particles (or aggregates) were studied to obtain the average particle size.

The transmittance spectra of the nanocoatings were measured by a UV–vis–NIR scanning spectrophotometer (Lambda 950, Perkin–Elmer Instruments, Waltham, MA, USA) with neat PMMA substrate as the reference. The haze values of the nanocoatings were evaluated using a haze meter (WGT-S, Shanghai Precision and Scientific Instrument, Shanghai, China) according to the standard GB/T 2410-2008.

The elastic modulus (E) and hardness (H) of the coating samples were evaluated with a nano-indenter (Nano Indenter XP, MTS Systems Co., Eden Prairie, MN, USA). A Berkovich tip (a three-sided pyramid tip) was utilized for the test. The experiments were conducted in continuous stiffness measurement (CSM) mode, and the maximum penetration depth was programmed to be 2 μm for all samples. The E and H values were averaged from five separate indents.

3. Results and discussion

3.1. Viscosity of dispersion

Fig. 1 shows the apparent viscosity of the dispersions containing silica nanoparticles and butyl acetate as a function of the milling