

Nanocomposite Fabrication Through Particle Surface Initiated Polymerization

Zhanhu Guo¹, Sung Park², H. Thomas Hahn¹

(1) Multifunctional Composite Lab, Mechanical & Aerospace Engineering Department,
University of California at Los Angeles, Los Angeles, CA 90095

(2) Advance Materials and Processes Technology, Northrop Grumman Corporation ISWR, El
Segundo, CA 90245

1. Introduction

Magnetic nanoparticles (NPs) have attracted much interest due to their special physicochemical properties such as enhanced magnetic moment¹ and coercivity² different from the bulk and atomic counterparts. Incorporation of the inorganic NPs into a polymer matrix has extended the particle applications such as in high-sensitivity chemical gas sensors³ due to the advantages of polymeric nanocomposites possessing high homogeneity, flexible processability and tunable physicochemical properties such as improved mechanical, magnetic and conductive properties.⁴⁻⁶ High particle loading and flexibility are required of nanocomposite for certain applications such as photovoltaic (solar) cells⁷, photodetectors and shape-memory devices⁸⁻⁹. A microwave absorber is another application that can benefit from using magnetic nanoparticles¹⁰⁻¹². A typical microwave absorber consists of micron size magnetic fillers in a polymer matrix. To get an optimum absorption, the particle loading in the polymer matrix is about 40% to 60% by volume. However, the challenge of incorporating nanoparticles into polymer is amplified by the difficulty of dispersing a high loading of nanoparticles without sacrificing the mechanical properties of the resulting composite. Current high-particle-loading nanocomposites are normally fabricated by directly mixing the particles with the polymer monomers followed by curing at a certain temperature, or alternatively, using a solvent to disperse the particles followed by casting to produce a thin film. Both methods result in inhomogeneous dispersion and unacceptable mechanical properties. The major challenge is to process a nanocomposite with uniform particle distribution and good properties.

In this study, nanoparticle surface initiated polymerization (SIP) method by utilizing the physicochemical adsorption of the initiator onto the nanoparticle surface in tetrahydrofuran solution was adopted to fabricate the magnetic nanoparticle filled polyurethane nanocomposite. The reaction mechanism was investigated by FT-IR spectrophotometer, thermo-gravimetric analysis (TGA), and TEM. The particle distribution was studied by SEM and AFM. The obtained iron-oxide nanoparticles filled polyurethane nanocomposite exhibits highly flexible as compared with the brittle and rigid ones obtained from the direct mixing method. The particle loading can be tuned to up to 60 wt%.

2. Experimental

Materials

The polymeric matrix used was a commercial, clear polyurethane coating (CAAPCOAT FP-002-55X, manufactured by the CAAP Co., Inc.), which contains two-part polyurethane monomers, i.e., 80 wt. % diisocyanate and 20 wt.% diol. The chemical structure of monomers is shown in Figure1. The liquid resin has a density of 0.83 g/cm³. Iron oxide (Fe₂O₃, Nanophase Technologies) nanoparticles with an average diameter of 23 nm and a specific

surface area of 45 m²/g were used as nanofillers for the nanocomposite fabrication. Polyurethane catalyst (a liquid containing ~20-65 wt.% aliphatic amine, 1-50 wt.% parachlorobenzotrifluoride and 10-35 wt.% methyl propyl ketone) and promoter (polyurethane STD-102, containing 1 wt.% organo-titanate and 99 wt.% acetone) were purchased from CAAP Co. Inc. Tetrahydrofuran (THF, anhydrous) was purchased from Aldrich-sigma Chemical Company. All the chemicals were used as-received without further treatment.

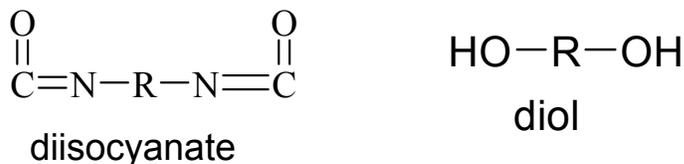


Figure 1. Schematic chemical structure of the used polyurethane two-part monomers

Nanocomposite Fabrication

The nanocomposites were fabricated by two different methods. One is the direct mixing (DM) and the other is based on the surface initiated polymerization (SIP). The fabrication procedures are as follows. In the DM method, 7.7 g monomers, 1.03 g catalyst and 1.42 g accelerator are added into 30 ml tetrahydrofuran (THF) solvent with ultrasonic stirring for 10 minutes. Then, 6.41 g nanoparticles are added into the above solution and ultrasonically stirred for 10 minutes. The suspended solution is poured out into a container for curing to obtain a nominal particle loading of 65%.

The SIP method starts with physicochemical adsorption of the initiator onto the iron-oxide (Fe₂O₃) nanoparticle surface in a THF solution. This will initiate the polymerization at the surface of particles. The surface initiated polymerization should serve dual advantages: separation of particles and improved mechanical strength. Since polyurethane polymer is chemically bonded directly onto the particle surface, an improved bond strength is expected compared to the one that the polymer just surrounding the particles. Also once polymerization is initiated from the surface, the particles won't be able to agglomerate due to the polymer chain surrounding the particles by steric force interactions, thus ensuring a good dispersion. Figure 2 depicts surface initiated polymerization.

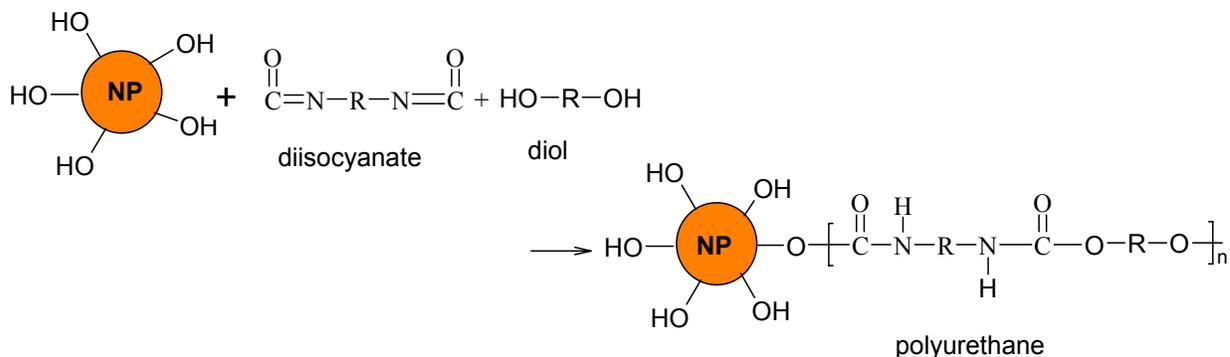


Figure 2. Surface Initiated Polymerization

To achieve this, the catalyst and accelerator are added into the THF solution containing nanoparticles and ultrasonically stirred for half an hour. The sonication offers evaporation of moisture that was physically adsorbed onto the particle. The monomers are then added into the above solution drop by drop within half an hour and the polymerization is left to continue for 6 hours. Finally, the solution is poured into a mold to evaporate the solvent. The resulting composite is pressed for about half an hour on a hot press at a temperature of 266 °F and a pressure of 10 psi.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded in the FT-IR spectrometer (Jasco, FT-IR 420) in transmission mode under dried nitrogen flow (10 cubic centimeters per minute, ccpm) conditions. The liquid mixture of catalyst and accelerating agent dispersant was mixed with powder KBr, ground and compressed into a pellet. Its spectrum was recorded as a reference to be compared with that of catalyst and accelerating agent treated nanoparticles.

Thermo-gravimetric analysis (TGA, PerkinElmer) from 25 °C to 600 °C with an argon flow rate of 50 ccpm and a heating rate of 10 °C/min was used to study thermal degradation of the nanocomposites. Particle dispersion in PU was characterized with scanning electron microscope (SEM, JEOL field emission scanning electron microscope, JSM-6700F).

The mechanical properties of the fabricated nanocomposites were evaluated by tensile tests following the American Society for Testing and Materials (ASTM, 2002, standard D 412-98a). The samples were prepared as standard described and a crosshead speed of 15 mm/min was used and strain (mm/mm) was calculated by dividing the crosshead displacement (mm) by the gage length (mm).

3. Result and Discussion

Physicochemical Analysis

The physicochemical attachment of catalyst-promoter (CP) mixture onto the particle surface was verified by TGA and FT-IR analyses. The sample was prepared by dispersing the NPs into the THF solvent, adding the exact amounts of catalyst and accelerator, stirring for half an hour, and washing the CP-treated nanoparticles with THF. The CP mixture is completely decomposed at temperatures around 200° C. The as-received nanoparticles show continuous weight loss possibly arising from the dehydration of the physicochemically adsorbed moisture; however the treated nanoparticles show a similar weight loss as the catalyst/accelerator mixture by itself. This also indicates that the physicochemically adsorbed moisture reacts with the CP mixture during sonication. The hot spots around the nanoparticle surface during sonication favor the loss of physically adsorbed moisture and promote reaction between the moisture and the CP mixture.

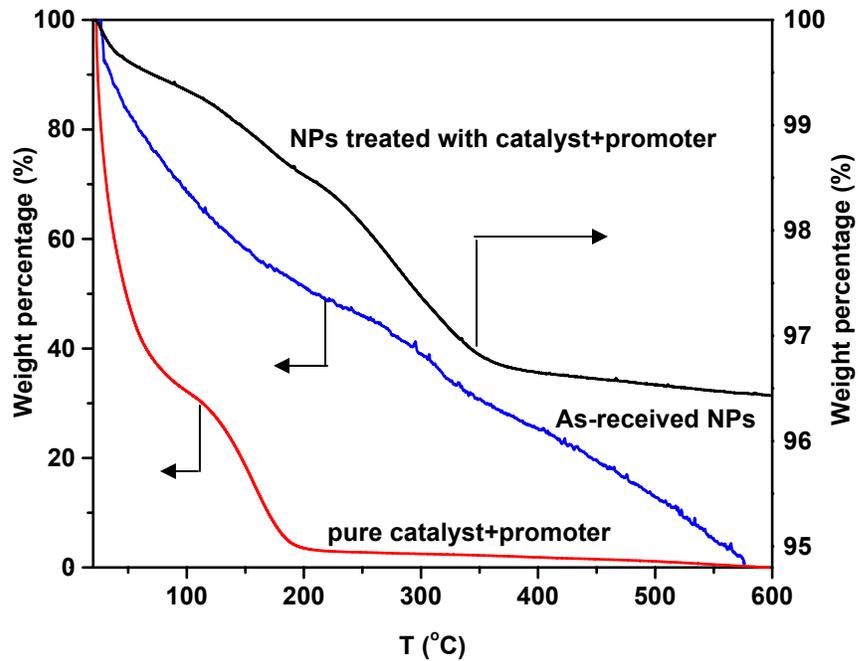


Figure 3. TGA of as-received nanoparticles, catalyst-promoter mixture, and treated nanoparticles

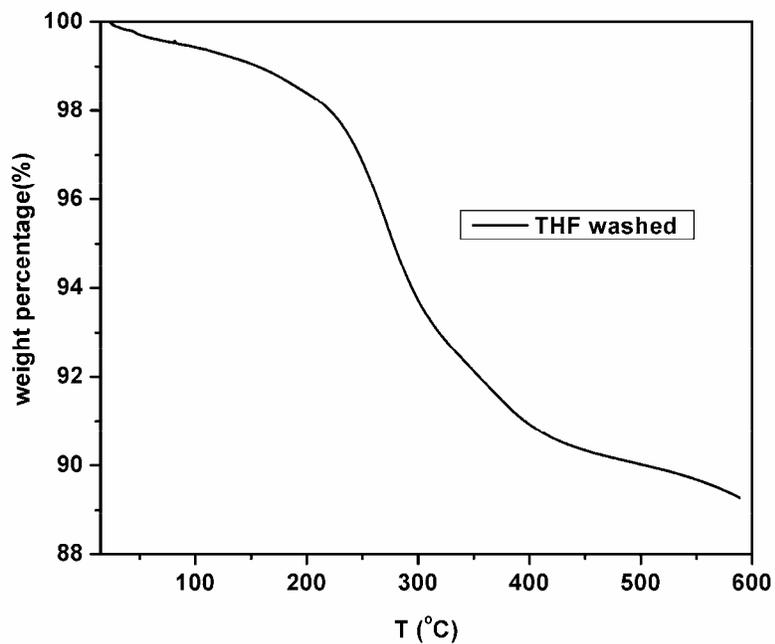


Figure 4. TGA of the PU-NPs after reaction for 6 hours and washed with excessive THF before pouring

In order to test the amount of polyurethane chemically bound onto the nanoparticle surface, the SIP particle suspension in THF solution was thoroughly washed with excess THF several times, dried under vacuum oven at room temperature, and tested on TGA, Figure 4. It is clear to see that about 8 wt.% PU is still present compared to 3.5 % for the treated NPs and 5% for as-received NPs in Figure 3. This is evidence indicating the chemical bond between the nanoparticle and the polyurethane matrix. Once polymerization is initiated from the surface of the particle, the extra polymer is linked by polymerization of the chemically bound polymer with the monomers.

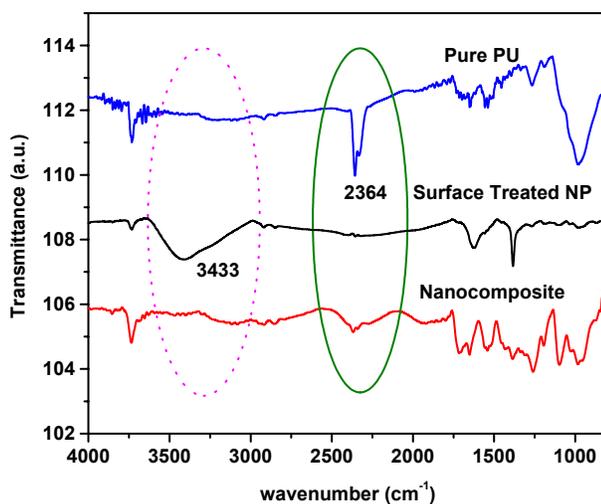


Figure 5. FT-IR spectra of neat polyurethane, as-received nanoparticles and nanocomposite

Further evidence of the CP mixture adsorbed onto the nanoparticle surface was shown in FT-IR. The FT-IR spectra shown in Figure 5 reveal dramatic differences in the transmittance properties before and after polymerization. The diisocyanate monomer is believed to react with the physicochemically adsorbed moisture (peak at 3433 cm⁻¹) on the nanoparticle surface with the aid of the CP mixture and further copolymerize with the diols to form a composite as shown in Figures 2.

Image Analysis

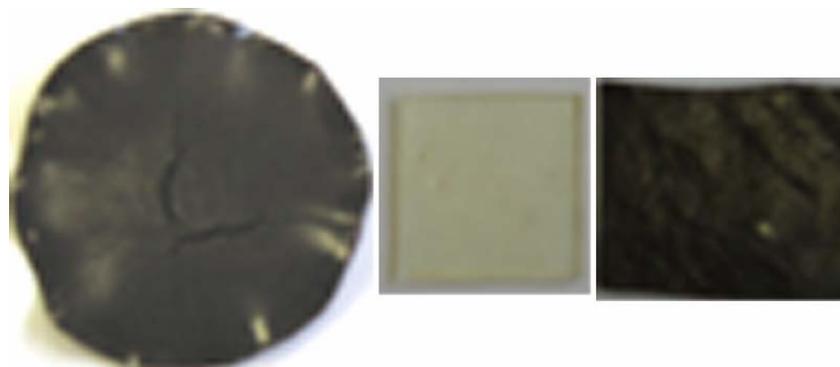


Figure 6. DM synthesized composite (left), pure cured polyurethane (middle) and SIP synthesized composite (right)

Figure 6 shows the image of the composites synthesized by the DM and SIP method, and the pure polyurethane, respectively. It is clear to see big cracks in the DM method fabricated composites. However, flexible and elastic rubber-like composite was observed in the SIP fabricated composites, which is similar to the pure cured polyurethane.

The scanning electron microscope was utilized to study the particle distribution. Homogeneous particle distribution within the polymer matrix further explains the surface initiated polymerization mechanism for the high-quality composite fabrication. As shown in Figure 6 (b) and (d), a clear sign of agglomeration is observed in the DM composite. However, discrete particles without obvious agglomeration are observed in the SIP composite, indicating that a good dispersion of nanoparticles can be obtained by the SIP process.

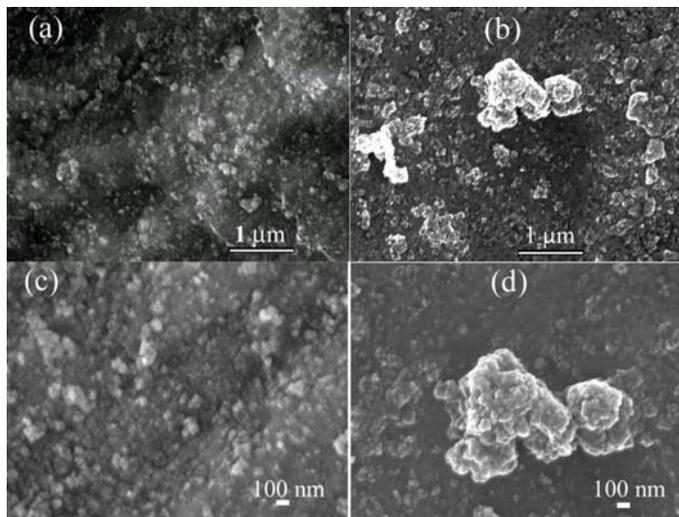


Figure 7. Scanning electron microscope of the composites by SIP method (a) magnification 22,000 and (c) 44,000; and DM method (b) low magnification 22,000 and (d) high magnification 44,000.

Mechanical Analysis

The flexibility of highly loaded composites was further evaluated by tensile test. The Young's moduli and tensile strengths are almost the same for both composites. However, the elongation of the SIP composite is about four times greater than that of the DM composite. The strong chemical bonding between the nanoparticles and the polyurethane polymer and uniform particle distribution within the polymer matrix are believed to contribute to the observed flexible behavior of the SIP composites.

Conclusion

The surface-initiated-polymerization (SIP) method was used to produce flexible iron oxide/polyurethane nanocomposites with a high particle loading. Chemical, thermal, mechanical, and image analyses were conducted to confirm that the SIP method yields improved structural integrity of the nanocomposites through better chemical bonding between the nanoparticles and the polymer matrix with uniform particle distribution. The SIP method thus opens a way to the fabrication of nanocomposites with high particle loading.

Acknowledgment

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