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Grafting from approach to the synthesis of photo-degrading polyurethane foams utilizing 2,2-dimethylolpropionic acid functionalized nano-TiO_2

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Waste polyurethane foams are becoming a serious environmental issue due to their low degradation rates upon environmental exposure. In order to accelerate foam degradation, this work examined a “grafting-from” method in which polyurethane (PU) chains were grown directly from functionalized TiO_2 nanoparticle surfaces. Both anatase and P25 TiO_2 nanoparticles were reached with 2,2-dimethylolpropionic acid (DMPA) to produce functionalized monomers, which were subsequently used for PU foaming in a “grafting-from” polymerization approach. The photodegradation rate and degradation mechanism of synthesized PU foams was examined by exposure of foams to a UV weathering chamber from 0 to 250 h with timed water spraying. The results show that anatase TiO_2 nanoparticles promote an increase in the degradation rate of polyurethane foams 120% over unmodified foam at an optimized loading of 3wt% DMPA-TiO_2(A). The presence of DMPA functionalized P25 nanoparticles produced an increase in the degradation rate of 66% over the unmodified foam at an optimized 1wt% loading. The results of this study suggest the potential for enhancing the degradation of polyurethane foams using a nano-TiO_2 functional monomer approach.

1. Introduction

Polyurethane (PU) foams are frequently used to produce durable goods for many everyday applications and industrial uses [1]. As such they enter the municipal solid waste stream by way of discarded consumer and industrial products. One major problem is that due to the irreversible cross-linking that occurs during the thermosetting process, commercial PU foams are not susceptible to facile degradation. On the other hand, PU recycling programs are currently limited to recycling clean scrap material from specific manufacturing processes, which are shredded and processed for use in various applications such as carpet underlay [2]. While a small number of chemical recycling processes do exist, they are extremely limited by high cost, the quality of material required for recycle, and the current lack of infrastructure. Hence, the possibility for enhanced degradation of PU's is of tremendous current interest [3–5].

Previous studies have examined the impact of UV irradiation on aromatic PU foams during UV exposure which have described the degradation process and yellowing of the foam [6–8]. Nano titanium dioxide (nTiO_2) has been shown to enhance the photodegradation of PU [9]. However, simple mixing approaches for integrating TiO_2 nanoparticles into polymers suffer from particle agglomeration, providing a limited enhancement in the degradation rate. One possible solution is “grafting-from” polymerization in which polymer chains are grown from a nanoparticle surface, providing steric stabilization and better access to the TiO_2 photocatalytic active sites. For instance, TiO_2 nanoparticles can be attached to a polyurethane matrix through NH_2 or OH functional groups [10,11]. However, it remains unexplored how this “grafting-from” approach will affect the photocatalytic activity of TiO_2 and the mode of photodegradation behavior.

In this study, 2,2-dimethylolpropionic acid (DMPA)-functionalized nano-TiO_2 molecules containing two hydroxyl groups were used to react with poly hexane diisocyanate (PMDI), providing a direct connection during nanocomposite formation (see Scheme 1). It was anticipated that the agglomeration using this approach would be decreased and that the TiO_2 nanoparticles chemically linked to the polyurethane structure would provide superior photocatalytic sites. By utilizing the photocatalytic properties of nano-

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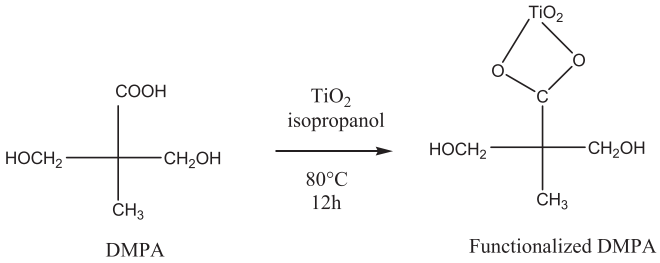

Scheme 1. Coordination of DMPA to the surface of $nTiO_2$.

TiO_2 (anatase or P25) [12–14], the decomposition rate of the polyurethane foam can be potentially enhanced when exposed to sunlight.

2. Materials and experiments

2.1. Materials

Polyols (Insulthane 200 part A) and PMDI (Insulthane 200 part B) were obtained from Line-X Coatings (Brantford, ON). 2,2-Dimethylolpropionic acid (DMPA) and anatase Titanium (IV) oxide nanopowder (TiO_2) with an average particle size less than 25 nm and P25 with an average particle size of 21 nm were purchased from Sigma–Aldrich (Mississauga, ON). All chemicals were used as received except DMPA which was heated under vacuum at 100 °C to remove any absorbed moisture.

2.2. Synthesis procedure

The synthesis of DMPA-TiO_2 and P25 follows a procedure previously described [11]. The coordination reaction occurs between the surface of DMPA and TiO_2 (Scheme 1). The polyurethane foam was prepared by direct mixing of commercial product PMDI and polyols with six samples of each type of nanoparticle prepared. Each sample was generated using 10 g of polyol (Insulthane 200 part A) and 10 g of PMDI (Insulthane 200 part B), and different amounts of DMPA-TiO_2 (anatase, P25), i.e.: 0.0 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g (0%, 1%, 2%, 3%, 4%, 5% by weight). The procedure is as follows: 10 g of PMDI was placed into a 150 ml polyethylene beaker, then mixed with DMPA-TiO_2 of different weights: 0.0 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g, and 1.0 g, under constant magnetic stirring at 600 rpm for 3 min at room temperature in order to reach a homogeneous solution. Then, 10 g of polyol was added with constant magnetic stirring at 600 rpm for 1 min to perform the foaming process. After that, the prepared PU/$nTiO_2$ foams were cured at room temperature for 24 h.

2.3. Characterization

The photoactivity of the as-prepared DMPA-TiO_2 was tested in 1 ppm methylene blue solution under UV irradiation in a light simulator (Luzchen ICH1) with a light intensity of 0.635 w/m^2. The methylene blue concentration was measured after 5, 10, 15, 20, 30, 40, and 60 min. Brunauer–Emmett–Teller (BET) surface area data was obtained using a Micromeritics Tri Star II 3020 instrument at 77 K. Prior to the N2 physisorption, the samples were degassed at 100 °C at reduced air pressure for 5 h. Fourier Transform Infrared (FTIR) spectroscopy was used to identify the functional groups of the prepared nanoparticles and polyurethane foams. FTIR analysis was performed using a NICOLET 6700 spectrometer which provided spectra in the range of 400–4000 cm^{-1} and was operated using 32 scans at 4 cm^{-1} resolution for each sample. Thermo-Gravimetric Analysis (TGA) analysis was performed to characterize the prepared nanoparticles and polyurethane foams using a TA Instruments® Q-series SDT Q600 analyzer. Data were analyzed using TA Instruments® Universal Analysis 2000 software. The aforementioned analyzer provided mass loss data over the temperature range of 25–800 °C at a constant heating rate of 20 °C/min in air. The photodegradation weight loss of PU/$nTiO_2$ foams were tested in a weathering chamber (Q-Sun Xenon Test Chamber) for 250 h. The test specimens had dimensions of 20 mm × 10 mm × 0.5 mm. The irradiation utilized was 0.55 w/m^2 which is equivalent to four noon summer sunlight. The temperature in the chamber was 65 °C with each cycle consisting of: 18 min irradiation plus water spray followed by 1 h 42 min irradiation. Scanning electron microscopy (SEM) was performed for the experimental nanocomposite thin foam slices before and after weathering using a LEO (Zeiss) 1540XB scanning electron microscope after each sample was osmium sputtered using an Edwards Auto500 unit. Osmium was deposited at 15 mA/min for 90 s to achieve a 5–7 nm osmium layer. All observations were made at 3 kV and varying magnifications.

3. Results and discussion

3.1. Polyurethane foam synthesis with DMPA-TiO_2(A) and DMPA-P25

As shown in Scheme 1, the nanoTiO_2 (anatase or P25) was treated with DMPA in isopropanol to make a functional monomer-i.e. $nTIO_2$-DMPA (see Scheme 1).

Functional group changes accompanying the coordination of DMPA with anatase TiO_2 can be observed using FTIR spectroscopy (Fig. 1). The hydroxyl group absorption at 3352 cm^{-1} from DMPA was broadened during nanocomposite formation. The absorption for a carboxylic acid group at 1683 cm^{-1} disappeared from the DMPA spectrum after functionalization, indicating no unreacted DMPA remained. There are no significant absorptions in the spectrum for anatase TiO_2 between 1400 and 1600 cm^{-1}. However, in the spectrum of functionalized TiO_2, there are three absorptions at 1558, 1471, and 1417 cm^{-1} which correspond to the presence of bidentate coordination interactions between titanium atoms and the carboxylic groups of DMPA (see inset). The identity of these absorptions has been confirmed by other studies [15,16].

From this functionalized DMPA monomer, polyurethane foams were synthesized through a “grafting-from” polymerization approach as shown in Scheme 2. In this methodology, the polyurethane chains were grown from the surface of the TiO_2 nanoparticles, which become embedded within the foam structure during the foaming process. Polyurethane foams containing both TiO_2 and DMPA-TiO_2 were prepared with the level of TiO_2 the same for both samples.

The SEM micrographs of polyurethane foams made by simple blending of $nTiO_2$ with those made using the “grafting-from” approach are compared in Fig. 2. It is clear that the “grafting from” approach using DMPA-TiO_2 provides a better dispersion of nanoparticles than those made by simple blending of $nTiO_2$ into the foam.

3.2. Polyurethane foam degradation kinetics

Langmuir–Hinshelwood kinetics is a widely used approach for modeling heterogeneous photocatalytic reaction processes [17]. In order to apply the Langmuir–Hinshelwood kinetics, some assumptions need to be made.

(1) Hydroxyl radicals are formed uniformly and immediately upon irradiation.