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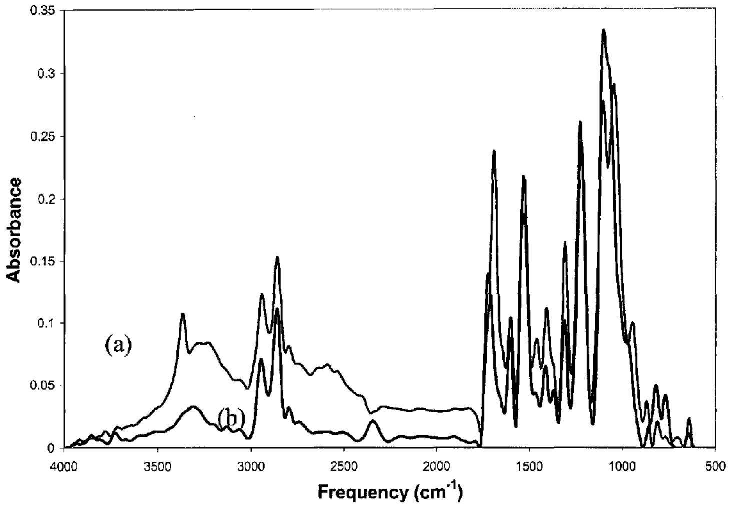

FIGURE 6

(57) **Abstract**: The present invention provides two methods for synthesizing novel titania-polyurethane (nTiO2-PU) nanocomposites for self-cleaning coatings, one a polymer functionalization method ("grafting to") and the other, a monomer functionalization method ("grafting from"). Here, 2,2 bis(hydroxymethyl) propionic acid (HMPA) was used as the coordination agent, which was reacted with n-TiO2 (50:50 anatase/rutile) to form nTiO2-HMPA, then polymerized in the monomer functionalization method. In the polymer functionalization method, HMPA was reacted with a pre-polymer to form the PU, and then subsequently reacted with n-TiO2 to form the polymer nanocomposite. The photocatalytic cleanability of the nanocomposites was investigated when exposed to ultraviolet radiation using additional unreacted HMPA or stearic acid as the model "dirt" compounds. Nanocomposites prepared using both strategies showed similar self-cleaning behavior, although the monomer technique gave less substrate degradation.

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SELF-CLEANING COATINGS

CROSS REFERENCE TO RELATED U.S APPLICATIONS

This patent application relates to, and claims the priority benefit of United States provisional patent application Serial No. 61/193,918 filed on January 8, 2009, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

The present invention relates to self-cleaning coatings produced from nanotitania-polyurethane ($nTiO_2$-PU) nanocomposites.

BACKGROUND TO THE INVENTION

Self-cleaning surfaces using nanostructured titania ($nTiO_2$) have been of significant recent academic and industrial interest, showing potential on glass surfaces providing antibacterial properties[1-3]. Research into TiO_2 as a photocatalyst semiconductor originally began in the early 1970's with the pioneering work of Honda and Fujishima who investigated the splitting of water into oxygen and hydrogen using TiO_2 irradiated by UV light [4]. Currently, TiO_2 photocatalysis is actively used in the field of photodegradation of organic compounds, specifically in environmental decontamination of air[5] and water [6]. Although most photocatalytic self-cleaning coating research has focused on self-cleaning glass,[7] self-cleaning polymers for paints and coatings are of significant potential industrial and scientific importance. However, little work has been performed on the chemistry for the integration of nano titania ($nTiO_2$) into polymers for self-cleaning coatings. As dirt and bacteria accumulate on almost every surface, nanocomposites that both strengthen the polymer, while providing self-cleaning behavior would be of significant interest.

Inorganic/organic hybrids are emerging materials for polymer coatings due to their extraordinary and unique combination of properties originating from the synergism between the inorganic nanoparticles and the polymer. Addition of a relatively small amount of the nanoparticles (e.g., less than 10 wt.%) dramatically changes the properties of the resulting polymer nanocomposite. As examples, $nTiO_2$ was used as a radiopacifier in dental composites and bone cements,[8, 9] as a solid plasticizer of polyethylene oxide (PEO) for lithium batteries,[10, 11] as a dye in a conjugated polymer for photoelectrochemical[12] or photoconductive[13] agents, and as a photocatalyst in a photodegradable TiO_2-polystyrene nanocomposite films[14].

Due to their extremely large surface-area/particle-size ratio, nanoparticles have a thermodynamic tendency to aggregate into clusters, reducing the resultant properties of the nanocomposite materials [15]. Many efforts have been taken in order to increase the nanoparticle dispersion and to enhance the filler-matrix interaction[16]. Increasing the dispersion of TiO_2 nanoparticles into a PVC polymer matrix was shown to increase the photocatalytic degradation significantly [17, 18]. One approach is breaking down the agglomerated nanoparticles using a mechanical method such as ultrasonic irradiation, which has been explored for dispersion of SiO_2, TiO_2, and Al_2O_3 nanoparticles during the synthesis of inorganic/polymer nanocomposite materials[19-21]. However, this approach is restricted due to the limited interaction between the inorganic fillers and the organic matrix, compared with the very strong interaction between individual nanoparticles.

An improved approach, termed "grafting to" or the polymer approach is modifying the surface of the inorganic filler with covalent attachment of the polymer chains minimizing agglomeration, while strengthening the interaction between the nanofiller and the polymer matrix. In a separate approach, the "grafting from" or monomer approach, polymer chains are grown from a nanosurface providing potentially higher graft densities and better control of the molecular weight and polydispersity of the polymer chains [22-25] .

It would therefore be advantageous to provide self-cleaning coatings which avoid the above-mentioned limitations.

SUMMARY OF THE INVENTION

Embodiments of the present invention provide a self-cleaning composition for application to surfaces, comprising titania-polymer ($nTiO_2$-P) nanocomposites, wherein said polymer is a step-growth polymer containing an HO-R(COOH)-OH type functionality.

In an embodiment of the present invention there is provided a self-cleaning composition for application to surfaces, comprising titania-polyurethane ($nTiO_2$-PU) nanocomposites.

The $nTiO_2$ includes titanium (IV) oxide nanoparticles ($nTiO_2$) and may have a composition with anatase:rutile ratios in a range from about 10:90 to about 90:10.

A preferred composition may have a composition which is about 50:50 anatase:rutile.

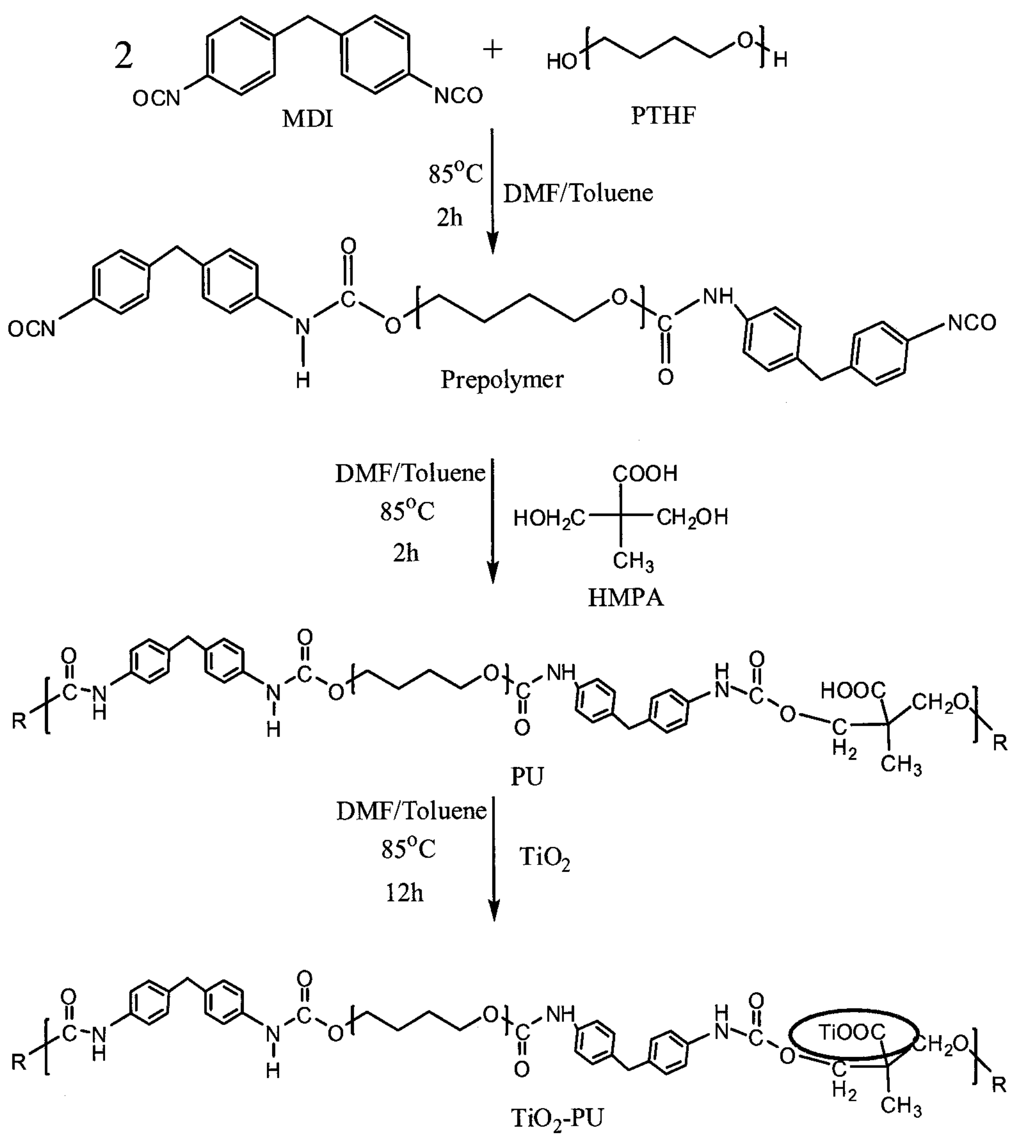
The nanoparticles may have an average particle size of in a range from about 1 nm to about 500 nm.

The $nTiO_2$ may be doped with one of transition metals, anions, zinc oxide, and any combination thereof. The transition metals may be any one or combination of Fe, Cr, V, N, Co, and the anions may be any one or combination of nitrogen, sulphur and fluorine anions.

The composition according to claim 1 produced by a method comprising the steps of:

a) reacting 4,4-methylene bis(p-pheyl isocyanate) with poly(tetrahydrofuran) to form a prepolymer, polymerizing the prepolymer in the presence of a chain extender 2,2-bis(hydroxymethyl)propionic acid to form polyurethane; and

b) reacting the polyurethane with TiO_2 nanoparticles at a desired wt.% to produce the titania-polyurethane ($nTiO_2$-PU) nanocomposites, following the scheme as follows:



The location of the linkage of the titania nanoparticle to the polymer backbone is shown circled.

In an alternative embodiment the composition may be produced by a method comprising the steps of:

a) reacting $nTiO_2$ with 2,2-bis(hydroxymethyl)propionic acid (HMPA) to produce a functionalized monomer, Ti-HMPA;

b) reacting 4,4-methylene bis(p-pheyl isocyanate) with poly(tetrahydrofuran) to form a diisocyanate terminated prepolymer, polymerizing; and

b) reacting the Ti-HMPA functionalized monomer with the diisocyanate terminated prepolymer as a chain extender to produce the titania-polyurethane ($nTiO_2$-PU) nanocomposites.

A further understanding of the functional and advantageous aspects of the invention can be realized by reference to the following detailed description and drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention will now be described, by way of example only, with reference to the drawings, in which:

Scheme 1 shows the synthesis route for synthesiss of segmented polyurethane and nanocomposite synthesis using the polymer approach ;

Scheme 2 shows the HMPA functionalization and subsequent nanocomposite synthesis using monomer approach;

Figure 1 shows in situ results for HMPA functionalization;

Figure 2 shows an FTIR Spectrum for optimized polyurethane elastomeric coating;

Figure 3 shows SEM-EDX titanium mapping of composite surfaces: left is SEM Image, right is EDX Image (a) 5wt% TiO_2-PU composite – monomer functionalization method (b) 5wt% tio_2-pu composite – polymer functionalization method, scale bar is 10 µm;

Figure 4 shows STEM images of 5wt% Ti-PU for (a) & (b) monomer functionalization method (3µm and 1µm scale, respectively) and (c) & (d) polymer functionalization method (3µm and 1µm scale, respectively);

Figure 5 shows comparative mass loss with respect to temperature for different concentrations and functionalization methods;

Figure 6 shows cleanability of HMPA from PU-TiO_2 Nanocomposites: (a) Before Irradiation, and (b) After 24 hrs. Irradiation;

Figure 7 shows FTIR cleanability results for 5 wt% nTiO_2-PU (Monomer method) contaminated with Stearic Acid (a) PU (b) nTiO_2-PU / Stearic Acid (0 min irradiation) (c) nTiO_2-PU / Stearic Acid (4000 min irradiation) (d) nTiO_2-PU / Stearic Acid (9000 min irradiation); and

Figure 8 shows FTIR cleanability results for 5 wt% nTiO_2-PU (Polymer method) contaminated with Stearic Acid (a) PU (b) nTiO_2-PU / Stearic Acid (0 min irradiation) (c) nTiO_2-PU / Stearic Acid (4000 min irradiation) (d) nTiO_2-PU / Stearic Acid (9000 min irradiation).

DETAILED DESCRIPTION OF THE INVENTION

Generally speaking, the embodiments described herein are directed to nanotitania-polyurethane (nTiO_2-PU) nanocomposites as self-cleaning coatings. As required, embodiments of the present invention are disclosed herein. However, the disclosed embodiments are merely exemplary, and it should be understood that the invention may be embodied in many various and alternative forms.

The figures are not to scale and some features may be exaggerated or minimized to show details of particular elements while related elements may have been eliminated to prevent obscuring novel aspects. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting but merely as a basis for the claims and as a representative basis for teaching one skilled in the art to variously employ the present invention. For purposes of teaching and not limitation, nanotitania-polyurethane ($nTiO_2$-PU) nanocomposites as self-cleaning coatings are disclosed herein.

As used herein, the terms “about”, and “approximately” when used in conjunction with ranges of dimensions, concentrations, temperatures or other physical or chemical properties or characteristics is meant to cover slight variations that may exist in the upper and lower limits of the ranges of properties/characteristics.

The present invention provides methods for making self-cleaning coatings based on TiO_2 and polyurethanes (PUs). Polymer nanocomposite films were prepared using two methods including “grafting to” and “grafting from” strategies with nanotitania ($nTiO_2$) and polyurethanes (PUs), which are well known polymers used in outdoor applications with excellent mechanical and weathering properties [26].

In an embodiment of the invention a 50:50 anatase/rutile mixture of $nTiO_2$ was used to provide both UV protection to the PU polymer from the rutile phase, and photocatalytic activity from the anatase phase of $nTiO_2$ [26] [27]. For increasing dispersion and enhancing the mechanical properties of the polymer, the inclusion of $nTiO_2$ into a polymer matrix requires that the fillers be chemically bonded to the PU polymer, which requires functionalization. Functionalization may be achieved by coordinating a carboxylic acid group with $nTiO_2$ [28, 29]. Hence, in embodiments of this invention 2,2, bis(hydroxymethyl) propionic acid (HMPA) was utilized, which has both 2 hydroxyl groups for reacting with the diisocyanate terminated pre-polymer, and a carboxyl group for coordination to $nTiO_2$. The produced nanocomposites exhibit self-cleaning behavior as deduced based on studies using added HMPA or stearic acid as the model compounds for "dirt", then photoirradiated to be described hereinafter.

The present invention will now be illustrated using the following non-limiting example.

Experimental

Materials.

All chemicals were purchased from Sigma-Aldrich (Mississauga, ON). 4,4-methylene bis(p-pheyl isocyanate) (MDI) was purified using hot filtration of the melt with Whatman 50 filter papers at a temperature of 65°C under vacuum. Poly(tetrahydrofuran) (PTHF) with an average molecular weight of 1000 Daltons was heated at 90°C under vacuum to remove all moisture. 2,2-bis(hydroxymethyl)propionic acid (HMPA) was washed and filtered under vacuum with distilled reagent plus methanol, and recrystallized under vacuum at 70°C.

Titanium (IV) oxide nanopower (nTiO_2) with an average particle size of 25 nm at 99.9% purity (50:50 anatase:rutile), Toluene anhydrous, 99.8%, dimethylformamide (DMF) ACS reagent, ≥99.8%, and tetrahydrofuran (THF) anhydrous, ≥99.9%, inhibitor-free were all used as received.

Polyurethane Nanocomposite Synthesis.

The polyurethane coatings were synthesized by a two-step process in DMF/toluene (50:50) at 85°C under nitrogen as shown in **Scheme 1**. In the first step (prepolymerization), MDI was reacted with PTHF at a molar ratio of 2:1 for 2 hours to create the prepolymer. The prepolymer was then polymerized for 2 hours at a 1:1 molar ratio with the chain extender, HMPA, for the polymer or "grafting to" technique. The synthesized PU was then reacted with the TiO_2 nanoparticles at the desired wt.% for 12 hours in DMF/Toluene at 85°C (**Scheme 1**).

For the monomer technique, 3.05g of $nTiO_2$ was reacted with 5.0g of HMPA in 100 mL of 2-propanol at 82°C under constant agitation and nitrogen gas for 12 h to produce the functionalized monomer Ti-HMPA (**Scheme 2**). HMPA was originally a white powder which turned to a yellowish crystalline powder after reaction with $nTiO_2$. The Ti-HMPA functionalized monomer was then reacted with the diisocyanate terminated prepolymer as the chain extender using the procedure previously described. As $nTiO_2$ was relatively insoluble, an increased reaction time of 4 h was required. Using the polymer and monomer methods, $nTiO_2$-PU composites were formed for subsequent stearic acid and HMPA cleaning studies. The final polymers were purified by methanol washing and poured onto Teflon plates, then heating at 80°C for 12 h under vacuum to form the nanocomposite films.

Characterization.

Fourier Transform Infrared (FTIR) spectroscopy using a Bruker® Vector 22 spectrometer with an MCT detector was operated using 32 scans at $4cm^{-1}$ resolution to identify the characteristic functional groups of the solid PU nanocomposite films, and the nanocomposites cleanability. To monitor the coordination of carboxylate groups to n-TiO_2, i*n situ* FT-IR monitoring of the solution concentration was performed using an immersion probe (Sentinel-Mettler Toledo AutoChem) in a stirred 100-mL autoclave (Parr Instruments). The DiComp ATR probe consists of a diamond wafer, a gold seal, a ZnSe support/focusing element, housed in alloy C-276. The probe was attached to an FT-IR spectrometer (Mettler Toledo AutoChem ReactIR 4000) via a mirrored optical conduit, connected to a computer, supported by ReactIR 2.21 software (MTAC). Spectra were recorded at a resolution of 2 cm^{-1} and the absorption spectra were the results of 64 scans.

TGA analysis was used for confirming the %TiO_2 in the nanocomposites and comparing their weight loss with temperature using a TA Instruments® Q-series TGA Q500 analyzer in the temperature range of 25 – 700°C at a constant heating rate of 20°C/min under N_2 for sample sizes ranging from 5 - 10mg. Scanning Electron Microscopy (SEM) images were recorded using a Hitachi® S-2600N instrument with each sample gold sputtered using a EMITCH® K550X deposited at 15 mA/min for 90 seconds to achieve a 5-7nm gold layer. All samples were taken at 5 kV at varying magnifications for different views. For full scale views, the magnification was taken at 350x and for the close up images, the magnification was 2500x and 4000x for HMPA and Ti-HMPA respectively. STEM was performed using a Hitachi HD2000 at 200 kV. Random sections of the PU and nancomposite coatings were sampled with the presented images representative of the surface. Energy Dispersive X-ray (EDX) detection was used to determine the approximate fractions of TiO_2 on the surface of the PU composite coatings, and to measure the dispersion of $nTiO_2$ within each sample. EDX measurements were performed using a Quartz Xone EDX scattering device attached to the Hitachi® S-2600N Scanning Electron Microscope after each sample was gold sputtered using the aforementioned technique.

Hydrophilic and hydrophobic behavior of the polymer nanocomposites was evaluated by contact angle goniometry using a Ramé-Hart Model 100 goniometer equipped with a micro-syringe system under ambient conditions using the sessile-drop method. 1 μL water droplet was dropped on the surface of the PU nanocomposite films using a micro-injector from 1 cm from the surface. Assuming spherical geometry of the sessile drop, the static contact angle was estimated by manual measurements at the vapor-liquid-solid interface using a reading microscope. It was also assumed that the composite surface were highly smooth, uniform and homogeneous to where the solid surface does not interact with the probe liquid. The results were repeated a minimum of 3X with both the mean and standard deviations reported.

Examination of self-cleaning behavior.

The self-cleaning photocatalytic properties of the PU and nanocomposite films were evaluated using both excess HMPA and stearic acid on the surface of the films under UV irradiation. The samples were dissolved in 50mL of THF and 20% HMPA, then poured onto a Teflon plate and dried under vacuum at 65°C for 24 hours. The samples were then irradiated perpendicular to the light source, at a constant distance of 10cm with a 20 W black light bulb. The UV intensity irradiated to the sample surface was given to be 0.8mW/cm^2 at the said distance using a 365±20 nm UV light source (model B100AP; UVP Inc.). During irradiation, air at room temperature was allowed to flow around the sample and the elimination of HMPA and stearic acid from the surface was determined using FTIR analysis. The sample thicknesses for all samples were between 90-110μm controlled using a constant surface area Teflon plate for a constant mass of 1.0g. **Results and Discussion**

Monomer Functionalization Method

For the monomer method, HMPA was reacted with nano titanium dioxide ($nTiO_2$) to form a functionalized monomer, termed Ti-HMPA, as shown in Scheme 2. The reaction of HMPA with $nTiO_2$ to form the Ti-HMPA monomer was examined using in situ FTIR spectroscopy, as shown in **Figure 1**. The characteristic peak at 1708cm^{-1} for the carbonyl group (C=O) stretch and the two C-O peaks at 1045cm^{-1} and 1225cm^{-1} in HMPA all decreased over a reaction time from 0-12 hours. This indicates that the functionalization reaction of HMPA removed the C=O and C-O groups, replacing them with coordination to $nTiO_2$. The small peak changes at 1410cm^{-1} and 1470cm^{-1} indicate some small changes in the titanium coordination peaks, further demonstrating functionalization. These results show that the coordination reaction took place in the first 12 hours, with no further reaction occurring in the remaining 12 hours.

Polyurethane Nanocomposite Synthesis

As illustrated in **Schemes 1** and **2**, $nTiO_2$/PU nanocomposites were synthesized using both the monomer ("grafting from") and polymer ("grafting to") techniques. The FTIR spectrums for the produced nanocomposite coatings showed all anticipated peaks[30] as shown in **Figure 2**, e.g. the NH peak at 3350cm^{-1}, the carbonyl peak at 1710cm^{-1} from the characteristic urethane linkage, and the lack of an isocyanate peak at 2265cm^{-1}. The spectrum for the prepolymer was not measured because the -NCO end groups react once introduced to humid air to form an aldehyde end group. The % of TiO_2 incorporated into the nanocomposites was confirmed by TGA (not shown). **Electron Microscopy of Nanocomposites**

In order to compare the "grafting from" and "grafting to" $nTiO_2$/PU samples, random sections of the coatings were sampled. **Figure 3** shows the SEM/EDX of the composite surfaces for (a) "grafting from" and (b) "grafting to" surfaces. Specifically, **Figure 3** shows the SEM-EDX titanium mapping of composite surfaces: Left is SEM Image, Right is EDX Image (**a**) 5wt% TiO_2-PU composite – monomer functionalization method (**b**) 5wt% TiO_2-PU composite – polymer functionalization method. The cale bar is 10 µm. The monomer "grafting from" technique gave much better dispersion of the nano titania particles in the PU matrix, and lowered TiO_2 agglomerate concentrations compared to the polymer "grafting to" method.

In order to examine the dispersion of $nTiO_2$ throughout the surface of the PU composite coatings in more detail, STEM images of the nanocomposite samples were taken for both the monomer functionalized and polymer functionalized coatings, as shown in **Figure 4**. TiO_2 nanoparticles incorporated into the polymer matrix appear both in the form of individual nanoparticles and small clusters of nano-sized agglomerates for the monomer functionalized $nTiO_2$-PU coating (**Figure 4a,b**), whereas the polymer functionalized $nTiO_2$-PU coatings have TiO_2 in micron-sized agglomerates (**Figure 4c,d**). Specifically, **Figure 4** shows STEM images of 5wt% Ti-PU for **(a)** and **(b)** monomer functionalization method (3µm and 1µm scale, respectively) and **(c)** and **(d)** polymer functionalization method (3µm and 1µm scale, respectively). This result shows that the monomer method gave much better dispersion of $nTiO_2$ and less agglomeration than that using the polymer method, further supporting the SEM/EDX results.

Wettability Results

Table 1 compares the contact angles of the PU and nanocomposite samples from the sessile drop measurements using Cassie's equation:

$$\cos\theta_{app} = f_1\cos\theta_1 + f_2\cos\theta_2 \tag{1}$$

where θ_{app} is the apparent contact angle, f_1 and f_2 are the apparent surface area fractions of TiO_2 and PU respectively, and θ_{app} is the average apparent contact angle. The contact angle for non-irradiated TiO_2 was assumed to be 30°.[1] The trend of Table 1 shows that the fraction of TiO_2 on the surface increases with increasing $nTiO_2$ content in the reaction mixture, and increases from the monomer synthesis (7.9%) to the polymer synthesis method (26.6%) for 5 wt% TiO_2.

Table 1
Contact Angles and calculations from Cassie's Equation for Polymer Nanocomposites.

Sample	$\theta_{app-comp}$	f_{TiO2}	f_{PU}
PU	93.6±1.82	0	1
5wt% $nTiO_2$-PU monomer functionalization	89.4±3.91	0.079	0.921
5wt% $nTiO_2$-PU polymer functionalization	79.4±2.07	0.266	0.734
10wt% $nTiO_2$-PU monomer functionalization	76.6±1.67	0.317	0.682
10wt% $nTiO_2$-PU polymer functionalization	72.6±1.14	0.390	0.610

In the reaction of both the polymer and monomer methods of functionalization, equal mass percentages of TiO_2 were used and formed in the polymer as confirmed by TGA. However, both the 5wt% and 10wt% $nTiO_2$-PU samples using the polymer functionalization method gave a lower contact angle than that from the monomer technique, and a higher weight % of TiO_2 on the surface, which was similar to the EDX results, as also observed by electron microscopy. This is attributed to phase separation between the hydrophilic TiO_2 nanoparticles and the hydrophobic PU polymer [31]. The phase separation is reduced using the monomer method, which helps creates a more hydrophobic TiO_2 surface providing better dispersion in the polymer matrix and better linkage to the polymer chains.

TGA Analysis

The effect of the two different methods of polymerization were studied using TGA analysis, as shown in **Figure 5** which shows comparative mass loss with respect to temperature for different concentrations and functionalization methods. At the crystalline hard segment decomposition temperature (over 275 °C), all $nTiO_2$-PU composite samples provided lower weight loss compared to the virgin PU sample, indicating enhanced stability of the nanocomposites with temperature. This **Figure** shows that increasing the mass percentage of n-TiO_2 in the polymer increases the thermal stability of the hard segment, thus increasing the thermal degradation temperature. This enhanced thermal behaviour is due to the ionic bonding between n-TiO_2 and the polymer chains, and ionic cross-linking formed through functionalization.

The TG curves show that the monomer method of functionalization “grafting from” improves the thermal stability to a greater extent at both 5 and 10 wt%, compared to the polymer method. This result is attributed to the increased dispersion of $nTiO_2$ throughout the PU and the enhanced linkage of the nanoparticles to the PU chains.

The polymer method does not break apart the $nTiO_2$ agglomerates as well, having larger groups of particles not functionalized within the matrix of the polymer. This can lead to phase separation between the polymer chains and the $nTiO_2$ particles, as shown by the contact angle results, decreasing the thermal properties[32]. Hence, as the monomer method decreases the size of the TiO_2 agglomerates and increases the amount of composite chain cross-linking; it provides better heat stability to the nanocomposite.

Cleanability Studies

FTIR analysis was utilized to demonstrate the cleanability of each of these surfaces where two different substances as models for "dirt" were deposited on the surface of the polymer coatings, i.e. excess HMPA (Mw ~ 134 g/mol), and stearic acid (Mw ~ 284 g/mol). **Figure 6** shows the cleanability of HMPA from PU-TiO_2 Nanocomposites: (a) Before Irradiation, and (b) After 24 hrs. Irradiation. **Figure 6** shows the individual spectra peaks of (a) the $nTiO_2$/PU composite with the excess HMPA mixed within the bulk of the polymer, and (b) the resulting surface spectra of the $nTiO_2$-PU composite after 24 hrs of irradiation. It is evident that the complete degradation of HMPA is seen by the disappearance of the OH peaks located between 3000-3600cm^{-1}, the carboxylic acid OH peaks located between 2500-3000cm^{-1} and a decrease in the C=O peak at 1710cm^{-1}; all three of which are the main characteristic peaks of HMPA. The FTIR analysis for the cleanability of the polymer and monomer functionalization methods with the addition of 20%

excess HMPA were found to provide identical results with the surface being cleaned within 24 hours of irradiation with a UV source of 365nm.

To further examine the cleaning differences between the two methods of functionalization, a larger more hydrophobic acid was used, i.e. stearic acid (Mw ~ 284 g/mol), which is a common model for "dirt". **Figure 7** shows FTIR cleanability results for 5 wt% $nTiO_2$-PU (Monomer method) contaminated with Stearic Acid (a) PU (b) $nTiO_2$-PU / Stearic Acid (0 min irradiation) (c) $nTiO_2$-PU / Stearic Acid (4000 min irradiation) (d) $nTiO_2$-PU / Stearic Acid (9000 min irradiation). **Figure 7** shows the photocatalytic cleanability of stearic acid on the surface of $nTiO_2$-PU composite coatings over a time frame of 0-9000 minutes produced by the monomer functionalization method. Stearic acid contains typical peaks for C=O stretch (~1700cm^{-1}), O-H stretch (~2500-3000cm^{-1} for a carboxylic acid), and C-H stretches (2800-3000cm^{-1}).

It can be seen that the degradation of stearic acid occurs after UV irradiation by the lowering of these peaks from 0 - 9000 minutes. Most of the cleaning occurs in the first 4000 minutes, with 9000 minutes providing essentially complete cleaning of stearic acid. Stearic acid takes considerably more time to be "cleaned" than HMPA, likely as HMPA is both a lower Mw material and more highly oxidized, hence making it easier to be degraded.

The polymer method (**Figure 8**) shows essentially identical cleaning results of stearic acid. However, it led to an additional small decreasing of the C-H stretch peaks at 2800cm^{-1} at 9000 minutes of UV irradiation, indicating possible degradation of the polymer substrate. By optimizing the anatase/rutile ratio for different polymers, the degradation of the polymer surface can be minimized.

As shown above, the present compositions may be formulated to be applied to a substrate surface as a self-cleaning coating. They may also be formulated as a foam using aromatic diisocyanates (e.g. toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI or polymeric MDI) In this application, the foams are sprayed onto surfaces using commercial spraying devices consisting of liquid MDIs and polyols (along with appropriate chain extenders, cross linkers, and surfactants) that are pumped from separate vessels, then mixed together in a spraying head and delivered through a heated nozzle onto a desired surface. The Ti-HMPA additive can be blended into the polyol tank, with the spraying ratios adjusted accordingly. Rigid pour in place and molded foams can similarly be produced using the aromatic diisocyanate and mixed with the polyol/Ti-HMPA mixture using common industrial procedures.

The compositions may also be formulated as an elastomer using aromatic diisocyanates. Usually elastomeric polyurethane materials have a higher solids content than the foam based ones, although they are of similar composition. As described in the above application, flexible elastomeric materials are commonly produced by spraying a liquid TDI or MDI with polyol that are joined in a mixing chamber of a spraying device and subsequently deposited onto a surface after exiting through a heated nozzle. Here the Ti-HMPA can be blended with the polyol/additive mixture and dispensed in the appropriate ratio (monomer approach).

The present compositions may be formulated as a paint or topcoat finish using aliphatic diisocyanates with nanotitania for the paint additive and subsequently sprayed, brushed or rolled. Common aliphatic diisocyantes include hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and H12-MDI which can be used for this purpose. The common two package approach can be used where the aliphatic polyisocyanate is mixed immediately prior to application with polyacrylate polyol resin containing material. The Ti-HMPA mixture can be added into the polyol package (monomer approach) or pre-polymer (polymer approach) with reactive chain ends. The Ti-HMPA can also be blended into a solvent based polyurethane paint application.

The compositions may be substantially optically transparent using aliphatic diisocyanates. Common aliphatic diisocyantes include hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and H12-MDI. Here the diisocyanates can be mixed with polols and either sprayed, brushed or rolled. The compositions may be applied to any substrate including, but not limited polymers, textiles, ceramic, cement, glass, metal, wood, paper, nanoparticles and nanofibres.

The composition properties can be adjusted to be either hydrophilic or hydrophobic depending on polymer and nanostructure composition. Increased hydrophobicity can be obtained by increasing the polyol chain length while increased hydrophilicity can be obtained by increasing the amount of Ti-HMPA additive.

The compositions may be formulated to exhibit antimicrobial properties as nano-titania is a well known photocatalyst that can produce superoxide radicals when exposed to sunlight that break down cell walls of bacteria, fungi, while disrupting viruses and other microbial agents.

The compositions may be substantially non-degradable to the polyurethane polymer by optimizing the ratio of rutile:anatase TiO_2.

Summary

Polymer nanocomposites, $nTiO_2$-PU, were prepared using both a monomer polymerization method 'grafting from' and a polymer polymerization method 'grafting to'. For the monomer method $nTiO_2$ was shown to react with HMPA to form $nTiO_2$-HMPA crystals, where the $nTiO_2$ were well dispersed. The functionalization via the monomer method was found to aid in the breaking up of the TiO_2 agglomerates, giving better dispersion than the polymer functionalization method. EDX and contact angle analysis showed that the monomer method gave a lower amount of TiO_2 on the surface, and more hydrophobic polymers. The TGA analysis showed that both polymerization techniques gave nanocomposites with better heat stability than the virgin PU although the monomer technique gave more heat stable nanocomposites compared to the polymer technique. Both techniques showed similar self-cleaning behavior when excess HMPA or stearic acid were added as models for dirt, with the monomer method showing less substrate degradation.

A self-cleaning composition for application to surfaces, comprising titania-polyurethane ($nTiO_2$-PU) nanocomposites has been disclosed, however it will be appreciated that the present invention is not restricted to this particular embodiment. For example, other step-growth polymers containing an HO-R(COOH)-OH type functionality can also be made self-cleaning using this approach containing a di, tri, or tetra alcohol, such as, but not limited to, polyesters, polycarbonates, polybenzoxazoles, and polysulfones.

Both titania and doped titania nanoparticles (doped using transition metals e.g. Fe, Cr, V, N, Co, or anions, e.g. Nitrogen, S, F, etc.) or Zinc Oxide may be used. As well encapsulating the TiO_2 with SiO_2 can be beneficial for photocatalysis. Anatase:Rutile ratios can be altered from about 10:90 to about 90:10. The $nTiO_2$ may have an average particle size of in a range from about 1 to about 500 nm of about 50:50 anatase:rutile.

As used herein, the terms “comprises”, “comprising”, “includes” and “including” are to be construed as being inclusive and open ended, and not exclusive. Specifically, when used in this specification including claims, the terms “comprises”, “comprising”, “includes” and “including” and variations thereof mean the specified features, steps or components are included. These terms are not to be interpreted to exclude the presence of other features, steps or components.

The foregoing description of the preferred embodiments of the invention has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiment illustrated. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.

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THEREFORE WHAT IS CLAIMED IS:

1. A composition comprising nanotitania-polyurethane ($nTiO_2$-PU) nanocomposites.

2. The composition according to claim 1 wherein said $nTiO_2$ includes titanium (IV) oxide nanoparticles ($nTiO_2$) having a composition with anatase:rutile ratios in a range from about 10:90 to about 90:10.

3. The composition according to claim 1 wherein said $nTiO_2$ includes titanium (IV) oxide nanoparticles ($nTiO_2$) having a composition 50:50 anatase:rutile.

4. The composition according to claim 1, 2 or 3 wherein said $nTiO_2$ nanoparticles have an average particle size of in a range from about 1 nm to about 500 nm.

5. The composition according to any one of claims 1 to 4 wherein said $nTiO_2$ nanoparticles have an average particle size of about 25 nm.

6. The composition according to any one of claims 1 to 5 wherein said $nTiO_2$ is doped with one of transition metals, anions, zinc oxide, and any combination thereof.

7. The composition according to claim 6 wherein said transition metals are selected from the group consisting of Fe, Cr, V, N, Co, and wherein said anions and selected from the group consisting of nitrogen, sulphur and fluorine anions.

8. The composition according to any one of claims 1 to 7 formulated to be applied to a substrate surface as a self-cleaning coating.

9. The composition according to any one of claims 1 to 7 formulated as a foam using aromatic diisocyanates.

10. The composition according to any one of claims 1 to 7 formulated as an elastomer using aromatic diisocyanates.

11. The composition according to any one of claims 1 to 7 formulated as a paint using aliphatic diisocyanates with nanotitania for a paint additive.

12. The composition according to claim 8 characterized in that the coating is substantially optically transparent using aliphatic diisocyanates.

13. The composition according to claim 8 wherein said substrate is any one of polymers, textiles, ceramic, cement, glass, metal, wood, paper, nanoparticles and nanofibres.

14. The composition according to any one of claims 1 to 13 characterized in that the composition is self-cleaning.

15. The composition according to any one of claims 1 to 13 characterized in that the composition properties can be either hydrophilic or hydrophobic depending on polymer and nanostructure composition.

16. The composition according to any one of claims 1 to 13 characterized in that the composition exhibits antimicrobial properties.

17. The composition according to any one of claims 1 to 13 characterized in that the composition is substantially non-degradable.

18. The composition according to claim 1 produced by a method comprising the steps of:

a) reacting 4,4-methylene bis(p-pheyl isocyanate) with poly(tetrahydrofuran) to form a prepolymer, polymerizing the prepolymer in the presence of a chain extender 2,2-bis(hydroxymethyl)propionic acid to form polyurethane; and

b) reacting the polyurethane with TiO_2 nanoparticles at a desired wt.% to produce the titania-polyurethane ($nTiO_2$-PU) nanocomposites.

19. The composition prepared according to the method of claim 18 wherein in step a) the 4,4-methylene bis(p-pheyl isocyanate) is reacted with the poly(tetrahydrofuran) at a molar ratio of about 2:1 for about 2 hours to produce the prepolymer; and wherein the prepolymer is polymerized for about 2 hours at about a 1:1 molar ratio with the chain extender 2,2-bis(hydroxymethyl)propionic acid.

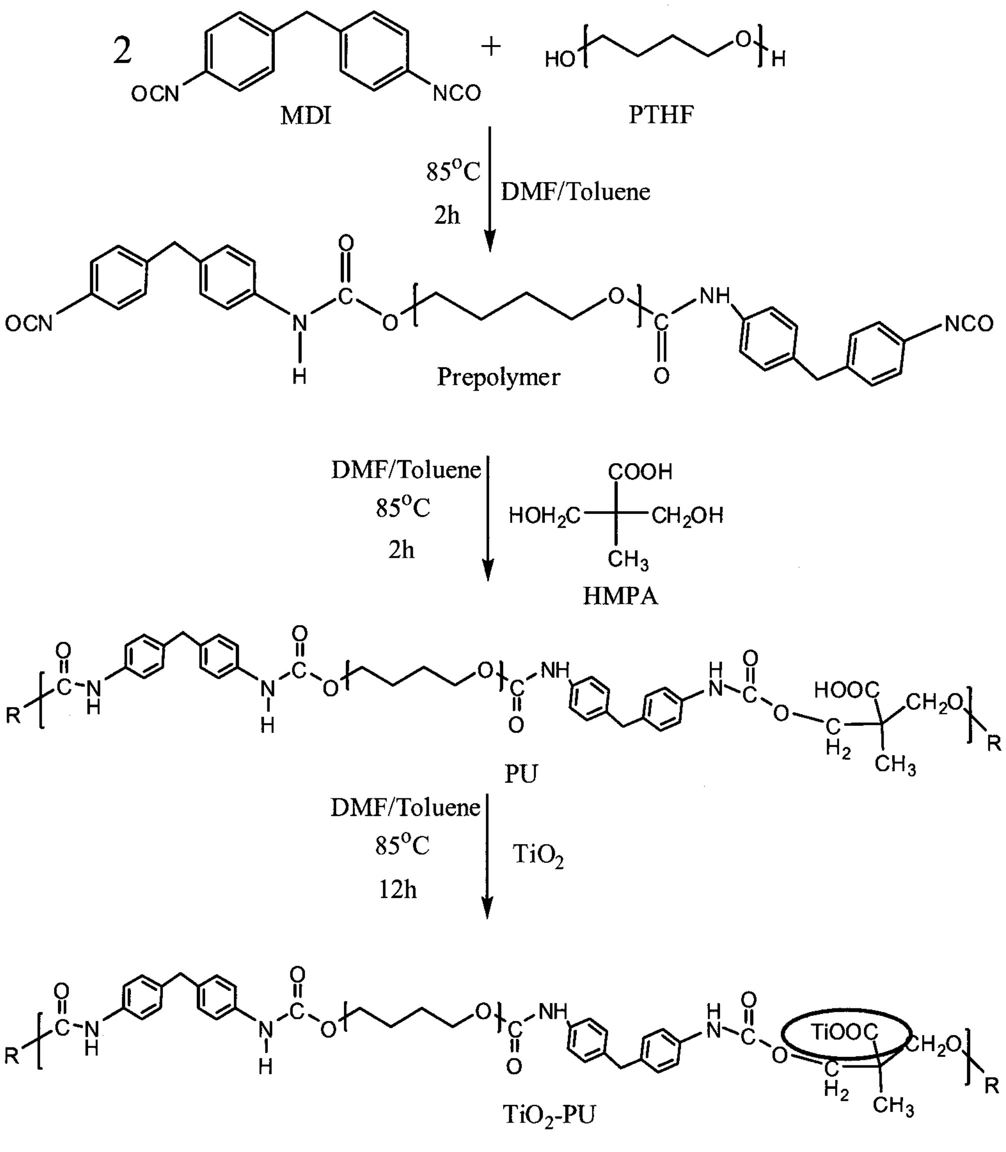
20. The composition prepared according to the method of claim 18 or 19 wherein in step b) the synthesized polyurethane is reacted with the TiO_2 nanoparticles at the desired wt.% for about 12 hours in dimethylformamide/toluene at about 85°C.

21. A self-cleaning composition for application to surfaces, comprising titania-polymer ($nTiO_2$-P) nanocomposites, wherein said polymer is a step-growth polymer containing an HO-R(COOH)-OH type functionality.

22. The composition according to claim 21 wherein said polymer contains a di, tri, or tetra alcohol.

23. The composition according to claim 21 or 22 wherein said polymer is selected from the group consisting of polyesters, polycarbonates, polybenzoxazoles, and polysulfones.

24. The composition according to claim 1 produced by a scheme as follows:



25. The composition according to claim 1 produced by a method comprising the steps of:

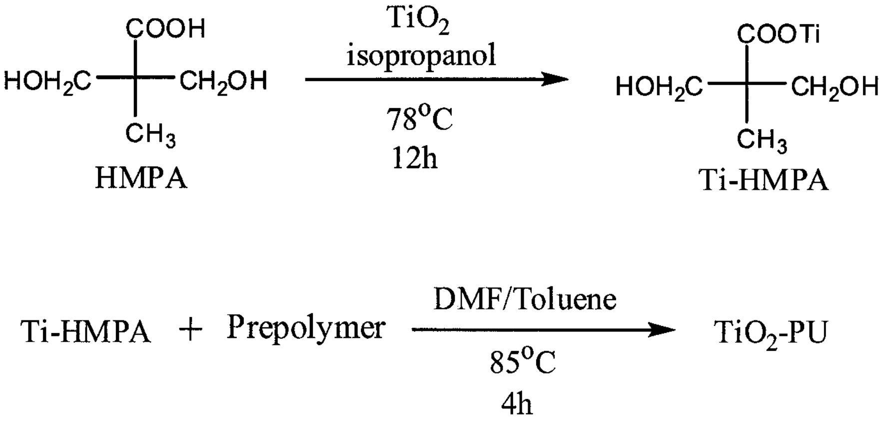
a) reacting $nTiO_2$ with 2,2-bis(hydroxymethyl)propionic acid (HMPA) to produce a functionalized monomer, Ti-HMPA;

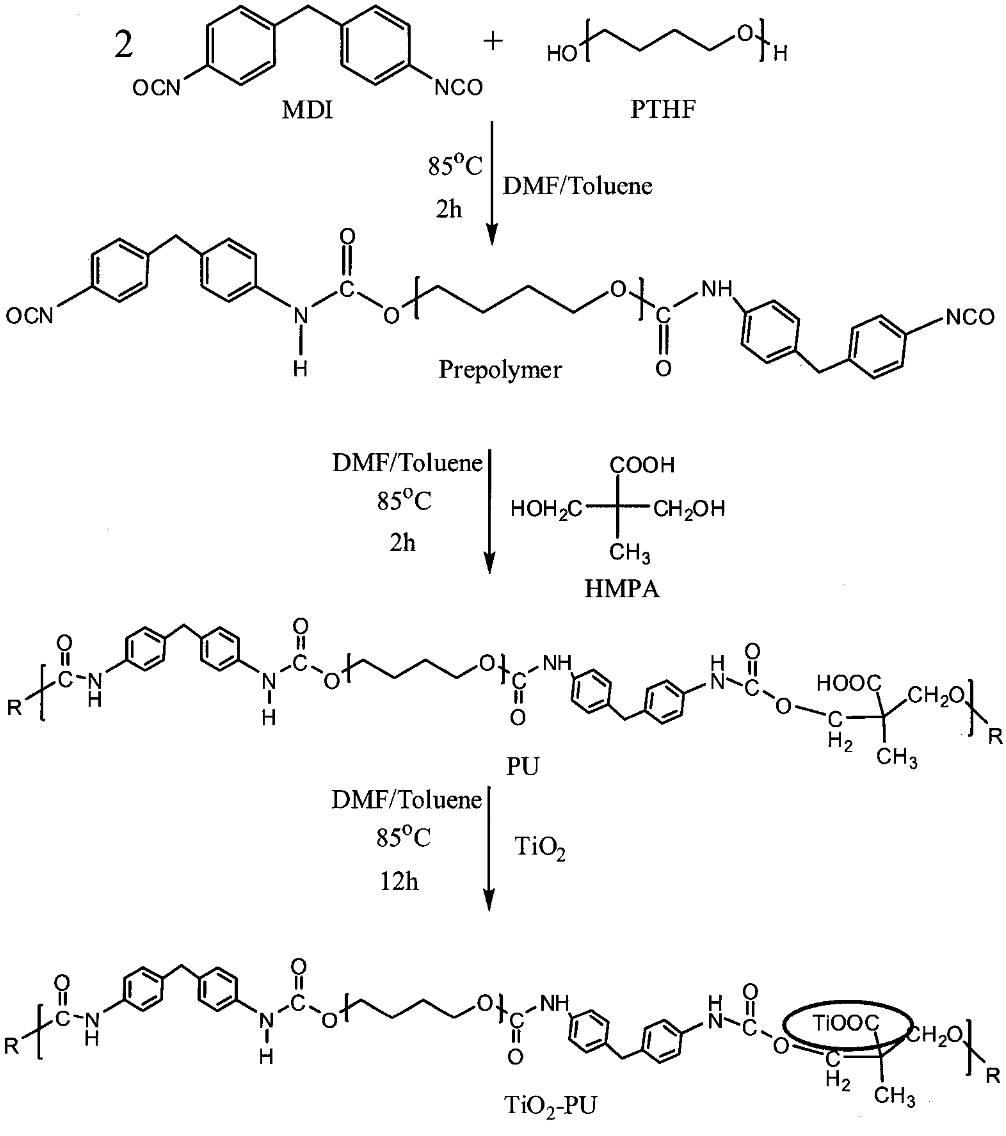
b) reacting 4,4-methylene bis(p-pheyl isocyanate) with poly(tetrahydrofuran) to form a diisocyanate terminated prepolymer, polymerizing; and

b) reacting the Ti-HMPA functionalized monomer with the diisocyanate terminated prepolymer as a chain extender to produce the titania-polyurethane ($nTiO_2$-PU) nanocomposites.

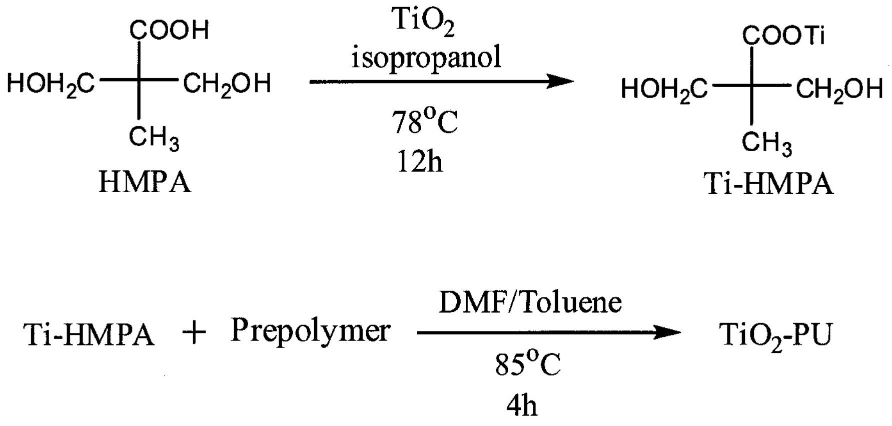
26. The composition prepared according to the method of claim 25 wherein in step a) the $nTiO_2$ is reacted with the 2,2-bis(hydroxymethyl)propionic acid in 2-propanol at about 82°C under constant agitation and nitrogen gas for about 12 h to produce the functionalized monomer Ti-HMPA.

27. The composition according to claim 1 produced by a scheme as follows:




2
OCN
NCO
MDI
+
HO
O
H
PTHF
85°C
2h
DMF/Toluene
Prepolymer
DMF/Toluene
85°C
2h
COOH
HOH2C
CH2OH
CH3
HMPA
PU
DMF/Toluene
85°C
12h
TiO2
TiOOC
TiO2-PU

Scheme 1


COOH
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CH2OH
CH3
HMPA
TiO2
isopropanol
78°C
12h
COOTi
HOH2C
CH2OH
CH3
Ti-HMPA
Ti-HMPA
Prepolymer
DMF/Toluene
85°C
4h
TiO2-PU

Scheme 2

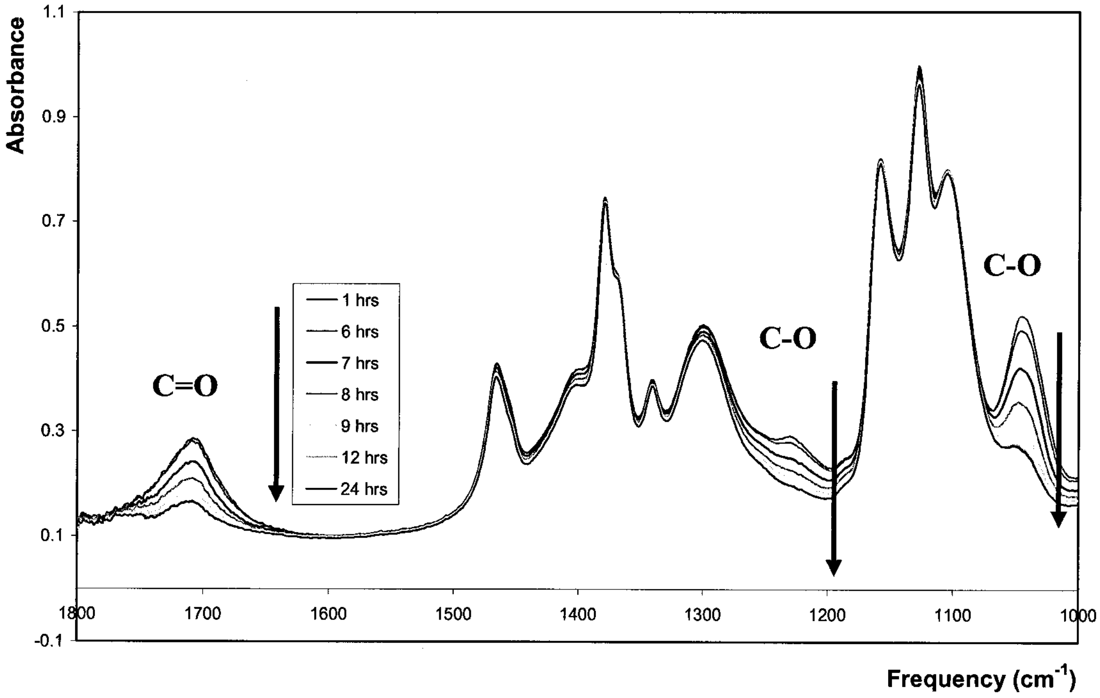
Absorbance
1.1
0.9
0.7
0.5
0.3
0.1
-0.1
1800
1700
1600
1500
1400
1300
1200
1100
1000
Frequency (cm^{-1})
C=O
C-O
C-O
1 hrs
6 hrs
7 hrs
8 hrs
9 hrs
12 hrs
24 hrs

FIGURE 1

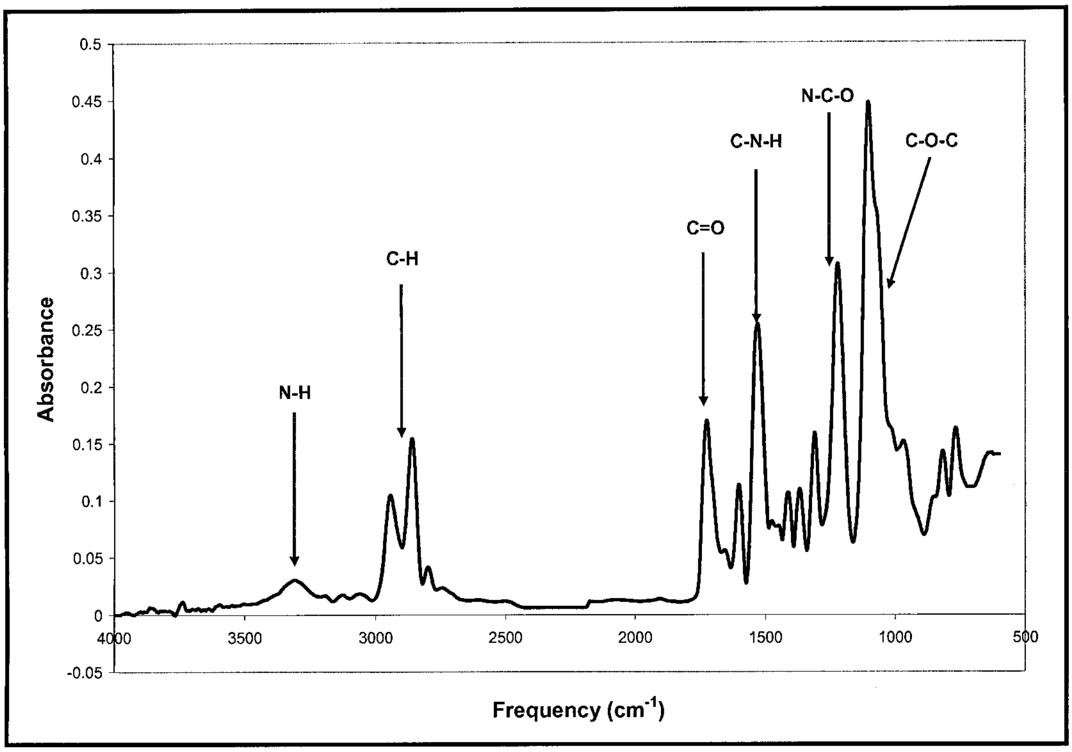

FIGURE 2

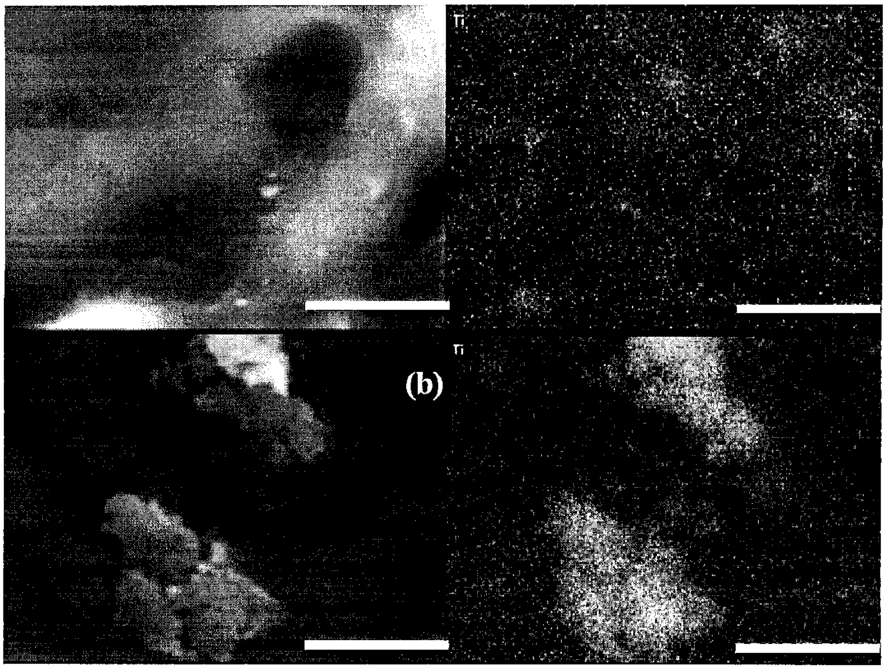

FIGURE 3

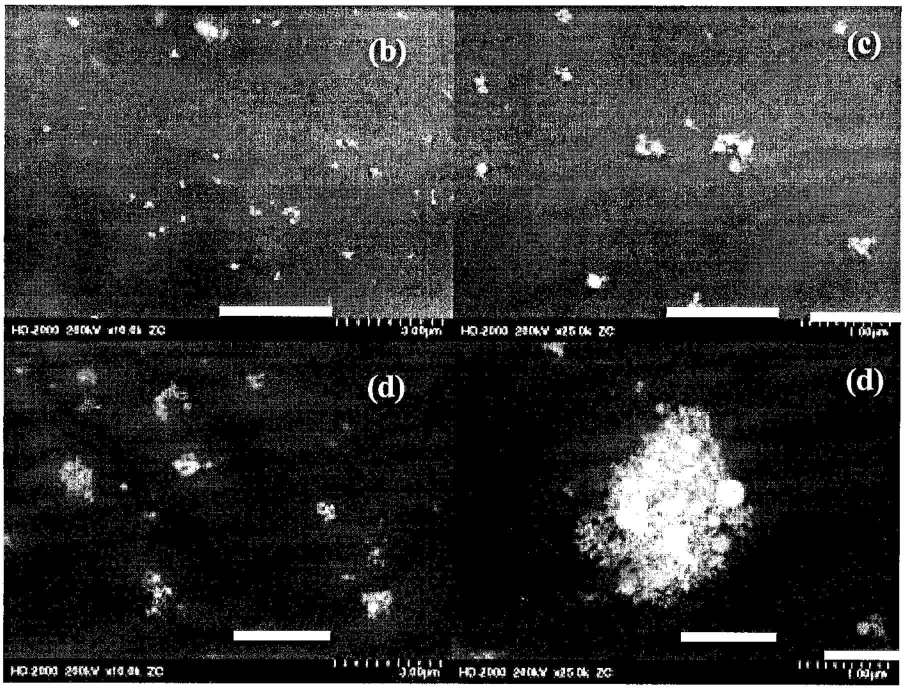
(b)
(c)
HD-2000 200kV x10.0k ZC
3.00μm
HD-2000 200kV x25.0k ZC
1.00μm
(d)
(d)
HD-2000 200kV x10.0k ZC
3.00μm
HD-2000 200kV x25.0k ZC
1.00μm

FIGURE 4

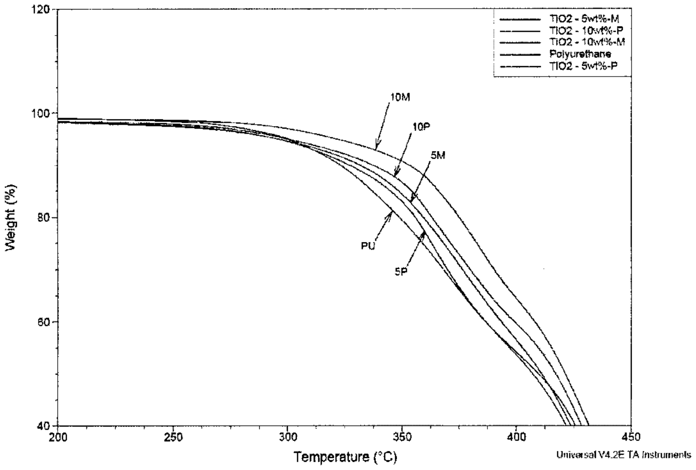

FIGURE 5

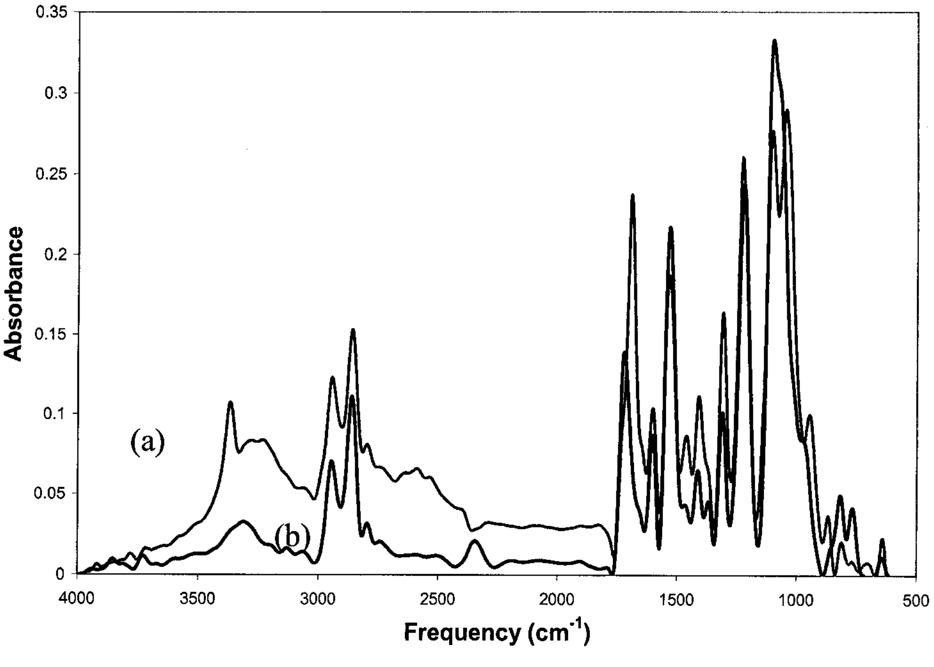

FIGURE 6

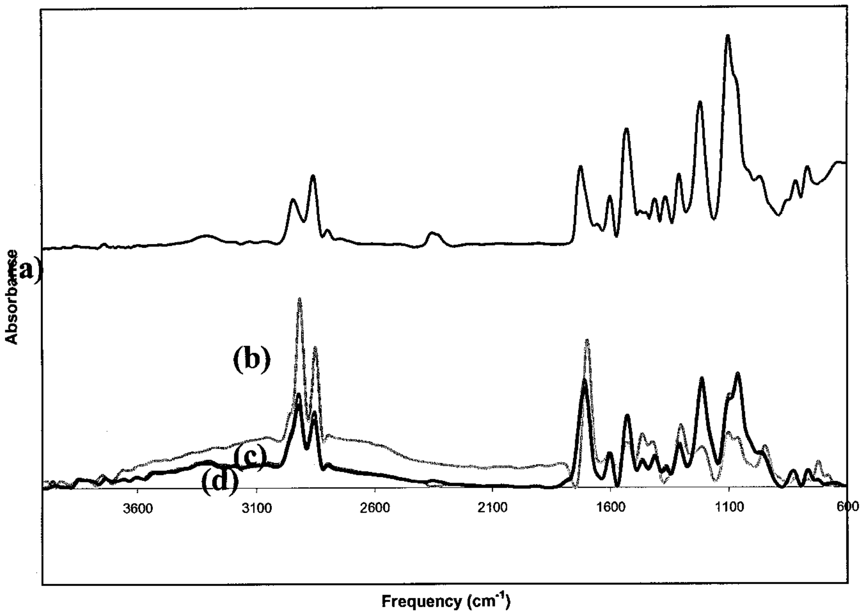

FIGURE 7

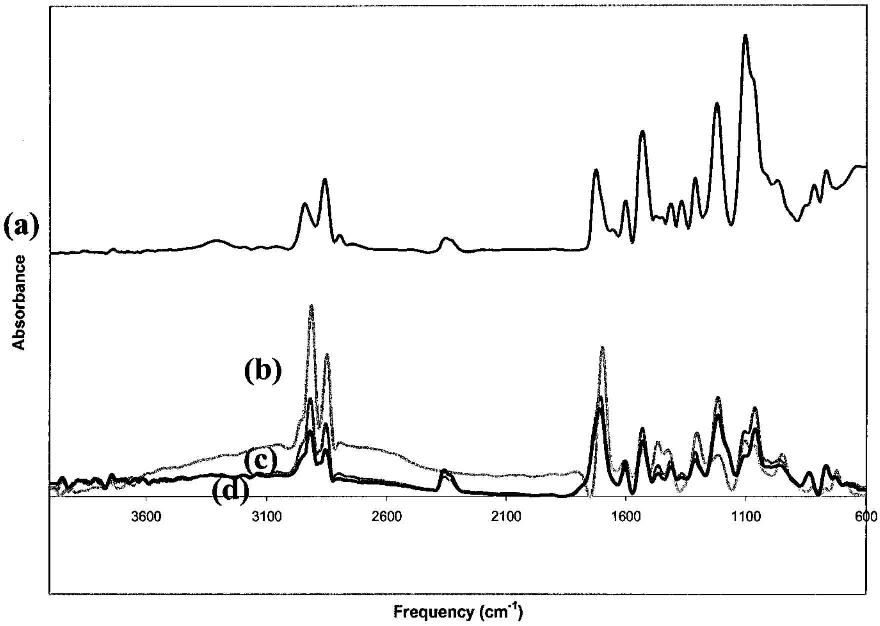

FIGURE 8