NANOPARTICLES DISPERSION IN PROCESSING NANOSTRUCTURE CHIRAL POLY(AMIDE-IMIDE)S BASED ON *N*-TRIMELLITYLIMIDO-*L*-LEUCINE/TiO₂ NANOCOMPOSITES: ALLOCATION AND PROPERTIES

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ABSTRACT

Poly(amide-imide)s (PAIs) as engineering materials have received more attention owing to their high thermal and chemical stability. Therefore, organic/inorganic nanocomposite (NC) of these materials has been widely studied in the last few decades. Here, we present PAI-NCs preparation containing surface modified TiO₂ nanoparticles (NPs) by employing silane coupling agent under ultrasonic process. Optically active nanostructure PAI was prepared from 5-(2-benzimidazole)-1,3-phenylenediamine (4) and chiral diacid monomer *N*-trimellitylimido-*L*-leucine (5) using molten salt tetrabutylammonium bromide as an activating medium. A considerable improvement of properties can be achieved by inserting NPs into the polymer matrix. The results of field emission scanning electron microscopy and transmission electron microscopy indicated that there is a little aggregation of a large quantity of particles. Thermogravimetric analysis confirmed that the heat stability of the polymer NCs in the temperature range of 400-800 °C was enhanced.

Keywords: Polymer nanocomposites, Molten salt ionic liquid, TiO₂ nanoparticles, Thermally stable poly (amide-imide), Ultrasonic irradiation

INTRODUCTION

Recent research in biodegradable polymers is related to with well-defined regions of utilization. But, biomedical applications of biodegradable and biocompatible macromolecules have produced a massive quantity of research and interest.¹ A wide variety of polymeric structures surrounding amino acids have been prepared and applied in structural, enzymological, and immunological studies, in addition to biomaterials.² It has been widely accepted that naturally occurring materials are very good sources for the synthesis of these macromolecules. Among the diverse natural resources that can be effortlessly attained, α -amino acids are highly promising.^{3,4}

Poly(amide-imide) (PAI) is a kind of thermoplastic resin with an acceptable high-temperature stability, outstanding mechanical properties, solvent resistance characteristics and excellent oxidative stability, which is typically linked with polyamides (PA)s and polyimides. All of these have helped PAI be mostly utilized with electronic materials, adhesives, fiber, film and composite materials. Therefore, the preparation, properties and applications of these materials have been widely described.⁵⁻⁹ Due to the introduction of flexible bridging groups in the PAIs backbone, these polymers are good candidates for utilization as matrixes in nanocomposites (NC)s. Therefore, the development of inorganic/organic NCs containing PAIs should be widely discussed to improve their properties.¹⁰⁻¹²

The assimilation of inorganic nanoparticles (NP)s into a polymer matrix brings about materials with improved properties as compared to both unfilled polymers and polymers filled with micrometric particles.^{13,14} These personalities typically arise from the synergistic effect, which is due to the addition of the nanofillers.¹⁵ However, customary fillers like talc, mica, calcium carbonate, silica, magnesium hydroxide, alumina, etc., makes it necessary for high loading quantities to attain a noteworthy enhanced performance. But, the weight augment of the final product is unwanted, in particular when compared to the light weight of macromolecules. To overcome the above disadvantage, throughout the last few decades, a new class of fillers in nanometer size range, preferably less than 100 nm, has been widely explored. The benefit of nanofillers is that they are miscible with the macromolecule matrix, utilizing inimitable synergisms between the combined materials.¹⁶⁻²⁰ These properties of macromolecules have had considerable developments owing to the incorporation of NPs. These properties are mechanical properties, e.g., strength, modulus and dimensional stability; decreased permeability to gases, water and hydrocarbons, thermal stability and heat distortion temperature, and optical clarity in comparison to conventionally filled polymers.¹⁶⁻²¹

Inorganic NPs, for instance, titanium dioxide (TiO₂) are inherently hydrophilic and in the case of utilizing them as filler, they are able to augment the hydrophilicity of the host macromolecule matrix. Furthermore, such additives, when they act as bonding (as hydrogen or covalent, i.e. coordination) with macromolecule functional groups, can encounter chain mobility; hence, they augment mechanical properties and thermal stability.^{22,23} Among many

NCs precursors, TiO₂ nanopowder is being explored ever more because of its stability, commercial availability, ease of preparation, non-toxicity, although it is chemically inert, low cost, corrosion resistant and has a high refractive index, UV filtration capacity and high hardness. Literature has as well illustrated that nanoscale TiO₂ reinforcement brings new optical, electrical, physiochemical properties achieved at very low TiO₂ content, making macromolecule TiO₂-NCs a new promising class of materials.²⁴ In addition, TiO₂ is believed to be a perfect option as catalyst for water treatment.²⁵ On the other hand, NCs that are based on TiO₂ and polymers have been broadly researched for the function of antibacterial application, degradation of organic pollutants, disposal of plastic waste, photo-electrochemical activity, solar energy conversion, photocatalysis, UV detectors, ultrasonic sensors, etc.²⁶⁻³³

Controlling the dispersal of nanoparticles in polymeric matrixes is the most important obstruction to the deposition of high-performance polymer NCs materials, resulting primarily from the strong inter-particle interactions.³⁴ Many efforts have been made to overcome this problem, such as surface modification of NPs with titanate and silane coupling agents,³⁵⁻³⁷ modification by chemisorption of small molecules,³⁸ modification by the adsorption of polymers³⁹ and ultrasonic irradiation during the synthesis of inorganic-polymer NCs materials.⁴⁰

Marand et al. reported the preparation of PAI/TiO₂ composite films (CF)s by an in situ sol-gel process. These CFs, having nanosized TiO₂ rich domains, were well disseminated within the PAI matrix. In comparison to the pure PAI, the PAI/TiO₂ CFs exhibited higher glass transition temperature, an upsurge and flattening of the rubbery plateau modulus, and a diminution in crystallinity.⁴¹ Also, Tsai et al. reported that the PAI/TiO₂ NC was effectively fabricated via in situ formation of TiO₂ within a PAI matrix. Thermal decomposition temperatures of PAI/TiO₂ NCs at 5 wt.% loss are above 460 °C.⁴² Ebert et al. investigated the effect of TiO₂ as inorganic filler in PAI membranes on various permeation processes. Furthermore, PAI membranes with 40 wt.% TiO₂ could endure a temperature treatment at 180 °C with only minor decrease in fluxes.⁴³

Recently, we have synthesized a variety of polymer NCs by the incorporation of TiO₂ NPs into polymer matrix for the preparation of bionanocomposite.⁴⁴⁻⁴⁶ As in our previous work, in this work, the aim of authors is the preparation of PAI-NCs containing natural amino acid that can introduce the optical activity and potential biodegradability in the resulting hybrid materials. The existence of amino acid moiety with multifunctional groups in the polymer backbone might cause better interaction with NPs. The objective of this work is the construction of novel PAI containing *L*-leucine moiety via direct polycondensation reaction in tetrabutylammonium bromide (TBAB) as a green media. Then dispersion of modified spherical TiO₂-NPs with the coupling agent in a PAI matrix was studied by means of an ultrasonic horn. The resulting polymer NCs were characterized by several techniques including Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and their morphology was investigated by field emission scanning electron microscopy (FE-SEM), and transmission

electron microscopy (TEM) analysis.

EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI, USA), Riedel-de Haen AG (Seelze, Germany), and Merck Chemical Co. (Darmstadt, Germany). TBAB (M.P. = 100-103 °C) was purchased from Merck Co. (Darmstadt, Germany) and used without further purification. 3,5-Dinitrobenzoyl chloride, 1,2-phenylenediamine, hydrazine monohydrate, phosphorus pentoxide (P_2O_5), and methanesulfonic acid (MSA) were obtained from commercial sources and used as-received. *L*-Leucine was utilized as obtained without additional purification. Chiral diacid monomer *N*-trimellitylimido-*L*-leucine was synthesized according to the previous works.⁴⁷ The coupling agent (3-aminopropyltriethoxysilane) (KH550) was obtained from Merck Chemical Co. Nanosized TiO_2 powder which contained mostly anatase form with a small percentage of rutile form was purchased from Nanosabz Co. with an average particle size of 30-50 nm.

Characterization

Infrared spectra of the samples were recorded at room temperature (R.T.) in the range of 4,000-400 cm^{-1} , on (Jasco-680, Japan) spectrophotometer. The spectra of solids were obtained using KBr pellets. The vibrational transition frequencies are reported in wave numbers (per centimeter). Band intensities are assigned as weak (w), medium (m), strong (s), and broad (br). Proton nuclear magnetic resonance (1H -NMR spectra, 400 MHz) was recorded in dimethylsulfoxide ($DMSO-d_6$) solution using a Bruker (Germany) Avance 400 instrument. Multiplicities of proton resonance were designated as singlet (s), doublet (d), doublet of doublet (dd) and multiplet (m). Inherent viscosity was measured by a standard procedure with a Cannon-Fenske (Mainz, Germany) routine viscometer. Specific rotation was measured with a Jasco (Osaka, Japan) P-1030 polarimeter at the concentration of 0.5 g/dL at 25 °C. TGA data were taken on STA503 WinTA instrument in a nitrogen atmosphere at a heating rate of 20 °C/min. The XRD patterns of the polymer and BNC polymers were recorded by employing a Philips X'PERT MPD diffractometer with a copper target at 40 kV and 30 mA and $Cu K\alpha$ radiation: $\lambda=1.54 \text{ \AA}$ in the range 10-80° at the speed of 0.05°/min. To clarify the nanoscale structure, TEM (CM 120, Philips) was also used at an accelerating voltage of 100 kV. For TEM, NCs were suspended in water and a small drop of suspension was deposited on the carbon coated copper grid. Surface morphology and sample homogeneity of NC polymers were characterized using FE-SEM (JSM-6700F, Japan). The reaction was occurred on a MISONIX ultrasonic liquid processor, XL-2000 SERIES. Ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly in the mixture solution system with a frequency of 2.25×10^4 Hz and 100 W powers.

Monomer synthesis

Construction of 5-(2-benzimidazole)-1,3-phenylenediamine (4)

At first, the dinitro intermediate 2-(3,5-dinitrophenyl)-benzimidazole (3) was attained by the direct condensation of 1,2-phenylenediamine (1) and 3,5-dinitrobenzoyl chloride (2) using MSA and P_2O_5 . In the second step, 5-(2-benzimidazole)-1,3-phenylenediamine (4) was achieved with hydrazine hydrate as the reducing agent and palladium as the catalyst.⁴⁸⁻⁵⁰

Construction of *N*-trimellitylimido-*L*-leucine (5)

Diacid monomer 5 was prepared by the condensation reaction of one equimolar of (trimellitic anhydride) TMA and one equimolar of the natural amino acid *L*-leucine in refluxing acetic acid according to our previous work.⁴⁷

Polymer synthesis

The PAI was prepared by diacid 5 and diamine 4 according to our previous work (Figure 1).⁵¹

Construction of PAI/ TiO_2 NCs

The PAI NCs were synthesized by mixing the suspension of a suitable quantity of TiO_2 powder modified with KH550 to yield 5, 10, 15 and 20 % W/W based on the PAI content, which was shadowed by irradiation with high-intensity ultrasonic wave for 4 h at R.T.³⁴ In this research, TiO_2 NPs were chemically modified via ultrasonic reaction to attain the KH550-capping TiO_2 particles (Figure 2). Figure 3 depicts a schematic model for the formation of the PAI NCs structure. A typical preparation process for PAI NCs is as follows: TiO_2 NPs (0.30 g) were added into acetone (10 ml), and 15 % weight percentage of KH550 was dissolved in H_2O (10 ml), which was maintained

under ultrasonication for 30 min. After that, it was centrifuged and dried. PAI was dispersed in 20 mL of absolute ethanol. A uniform suspension was gained after ultrasonication for 15 min at R.T. After irradiation, the precipitated powder was centrifuged and washed with absolute ethanol until the filtrate became colorless. The solid was dehydrated in a vacuum at R.T. for 8 h and the attained product was earmarked for added characterization. The weight concentration of the TiO_2 NPs varied from 5 to 20% in the polymer matrix.

Figure 1: Polycondensation reactions of diamine 4 with diacid 5 in molten TBAB.

Figure 2: Modification of TiO_2 NPs

Figure 3: Preparation of PAI/TiO₂ NCs.

RESULTS AND DISCUSSION

Polymer synthesis

The direct polycondensation of a dicarboxylic acid and diamine is one of the well-known methods for the fabrication of PAI. Solution polymerization reactions of an equimolar mixture of monomer 5, with diamine 4 in the presence of molten TBAB, were utilized to provide PAI, as shown in Figure 1. The obtained PAI is in yellow. In this study, molten TBAB was used as a solvent which is green, safe, and cost effective. Thus, TBAB acts both as an effective solvent and catalyst to mediate clean polymerization reactions and yield the desired PAIs. This methodology required only a small amount of the molten salt to promote the polymerization. The incorporation of chiral units into the polymer backbone was obtained by measuring the specific rotation of polymer. This showed optical rotation and therefore optical activity.⁵¹

Preparation of PAI/TiO₂ NCs

In the present study, we successfully prepared a series of PAI NCs by dispersing the nano-TiO₂ powder into the PAI matrix at R.T. In the first step, surface-modification of the nano-TiO₂ was performed to achieve the suitable dispersion of NPs within polymer matrix and yield a better compatibility between the NPs and host polymeric materials. On the other hand, this method modified the limited interaction between the inorganic materials and the polymeric matrix, as compared with the very strong interaction between individual NPs. The ultrasonic irradiation was utilized to break down the NPs agglomerates and improve the dispersivity of nanosized TiO₂ in polymer matrix.

Herein sonochemical reaction was employed for the preparation of TiO₂-KH550 modified NP. The sonochemical reaction supplies appropriate reaction temperature to accelerate the hydrolysis of KH550. Under these conditions, the collision chance of KH550 anchored onto the surface of TiO₂ sol particles is greatly increased.⁵² Silanol groups of KH550 generated by hydrolysis can interact with hydroxyl groups on the TiO₂ surface and form the modification layer with -NH₂ groups. The resulting PAI has lots of polar groups such as carbonyl, nitrogen and sulfur; the modified NPs might be dispersed absolutely and combined with PAI by different connections such as hydrogen bond, and also short-ranged steric and electrical interactions. Under ultrasonic irradiation,

the aggregates of nano-TiO₂ were broken down. Dispersion of NPs in the polymer matrix can be observed from the photographs of TEM and FE-SEM.

Infrared study

The FT-IR spectra of the chemically prepared pure PAI (a) and PAI/TiO₂ NC (5 wt%) (b), PAI/TiO₂ NC (10 wt%) (c), PAI/TiO₂ NC (15 wt%) (d), and PAI/TiO₂ NC (20 wt%) (e) are illustrated in Figure 4. The comparison of FT-IR spectrum of the modified and unmodified TiO₂ NPs revealed that the new bands appeared at 2870-2928 cm⁻¹. This can be attributed to C-H stretching band of γ -aminopropyl groups of KH550. Both of them show that the broad peak at 3400 cm⁻¹ corresponds to stretching motions of the surface hydroxyl or the adsorption water, the peak at 1630 cm⁻¹ to vibration of O-H bonds on the TiO₂ particles' surface and the broad band observed in the region 450-800 cm⁻¹ to Ti-O stretching peak.⁵³ From these data, it can be deduced that the silane coupling agent KH550 has been grafted on the surface of TiO₂ nanoparticles.

In the spectrum of original TiO₂, OH stretching band and bending band are observed at 3422 cm⁻¹. As a result, the presence of KH550 on the surface of TiO₂ was confirmed by the characteristic peaks of CH stretching band at 2871-2927 cm⁻¹ in the infrared data of KH550-modified-TiO₂ NPs, as compared to the infrared data of pure TiO₂. The observed broader bands at 3500 and 3422 cm⁻¹ were attributed to hydroxyl groups on different sites and some varying interactions between hydroxyl groups on TiO₂, respectively.⁵⁴ A broad absorption peak at 500-800 cm⁻¹ is assigned to the Ti-O-Ti stretching band. The N-H bending vibration of primary amine is observed around 1617 cm⁻¹. In addition, the broad band around 1084 cm⁻¹ corresponded to Si-O-Si bond observed, indicating the condensation reaction between silanol groups. It is assumed that KH550 adheres to the nano-TiO₂ particles possibly by coating. FT-IR spectrum of PAI/TiO₂ NC (15 wt%) is shown in Figure 4 (d), where the characteristic peaks of pure PAI and TiO₂ are still maintained. It may be proved that the structure of PAI was affected by the presence of TiO₂.

Figure 4: FT-IR spectra of (a) Pure PAI, (b) PAI/TiO₂ NC (5 wt%), (c) PAI/TiO₂ NC (10 wt%), (d) PAI/TiO₂ NC (15 wt%), (e) PAI/TiO₂ NC (20 wt%).

FT-IR spectra of NCs with different amounts of TiO₂ (5, 10, 15, 20 wt%) NPs (Figure 4) show the intensity of Ti-O-Ti stretching band is raised with an increase in TiO₂ NPs content in PAI.

X-ray diffraction data

XRD curves of pure PAI (a), pure TiO₂ (b), PAI/TiO₂ NC (5 wt%) (c), and PAI/TiO₂ NC (15 wt%) (d) are shown in Figure 5. The broad peak in the region of $2\theta = 10-30^\circ$ in XRD curve of pure PAI shows that PAI prepared in the absence of TiO₂ NPs is amorphous. Figure 5 (b) shows anatase and rutile phase for pure TiO₂ nano particles. The XRD patterns of PAI/TiO₂ NC (c) and (d) show characteristic peaks of anatase and rutile of TiO₂, indicating that the

crystallinity form of TiO₂ NPs has not been disturbed during the process. Also, the broad weak diffraction peak of PAI still exists, but its intensity decreases. It implies that the composite sample has a more ordered arrangement than the bare polymer, owing to the TiO₂.

Figure 5: XRD curves of (a) pure PAI (b) pure TiO₂ NPs (c) PAI/TiO₂ NC (5 wt%), and (d) PAI/TiO₂ NC (15 wt%).

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

The average crystalline size of nano-TiO₂, which is determined from the half-width of the diffraction using the Debye-Scherrer equation, is approximately 24 nm for PAI/TiO₂ NC (15 wt%) and 22 nm for PAI/TiO₂ NC (5 wt%) from peak (200). Scherrer's equation is as follows:

Where D is the crystallite size, λ is wavelength of the radiation, θ is the Bragg's angle and β is the full width at half maximum.⁵⁵

Morphology observation

FE-SEM micrographs of PAI/TiO₂ NC (5 wt%) (a, b), PAI/TiO₂ NC (10 wt%) (c, d), PAI/TiO₂ NC (15 wt%) (e, f), PAI/TiO₂ NC (20 wt%) (g, h) are exhibited in Figure 6. It presents a homogeneous microstructure, confirming that the TiO₂ NPs appear on the PAI surface in nanoscale.

TEM has proven to be a powerful tool for studying the distribution of nanofillers embedded within a polymer matrix. Typical TEM images for PAI/TiO₂ NC (10 wt%) are shown in Figure 7. TEM micrographs confirmed some individual domains of TiO₂ NPs in the PAI matrix. From these TEM results, it is clear that the surface modification of TiO₂ NPs in most cases will prevent their aggregation in the PAI matrix. But some aggregation was also observed.

Figure 6: FE-SEM micrographs of (5, 10, 15, 20 wt%), a and b: PAI/TiO₂ NC 5 wt%, c and d: PAI/TiO₂ NC 10 wt%, e and f: PAI/TiO₂ NC 15 wt%, g and h: PAI/TiO₂ NC 20 wt%.

Figure 7: TEM micrographs of PAI/TiO₂ NC (10 wt%).

Thermal properties

The thermal performance of manufactured NCs, as determined with TGA at a heating rate of 20 °C/min under a nitrogen atmosphere, is shown in Figure 8. The thermal stability of neat PAI and NCs at different particle contents can be seen in this figure. Table 1 demonstrates the corresponding thermoanalysis data, including the temperatures at which 5 % (T₅) and 10 % (T₁₀) degradation occur. The residue at 800 °C (char yield) and also, limiting oxygen index (LOI), based on Van Krevelen and Hoftzyer equation, were determined from the original thermograms.⁵⁶

$$\text{LOI} = 17.5 + 0.4 \text{ CR}$$

Where CR = char yield.

As shown in Figure 8, the obtained NCs have a rather good thermal resistance. From these data, it is clear that the introduction of TiO₂ NPs in polymer matrix causes the better thermal stability. However, the initial temperature of the NCs weight loss was not increased considerably with increasing TiO₂ content. From this data, it is clear that the addition of TiO₂

NPs into polymer matrix for PAI/TiO₂ NC (5 wt%) has the higher additional thermal stability. For TGA curves shown, the thermal stability of NCs was weakly increased as consequence of TiO₂ NPs and high melting point incorporation into the polymer matrix. The rate of decomposition of NCs was decreased slightly, showing that the polymer chains movements during heating are restricted by the introduction of TiO₂ NPs that can serve as a good thermal cover layer. Also, TiO₂ NPs offer a larger surface area and enhance the effect of thermal cover.²⁵

Table 1: Thermal properties of the PAI and PAI/TiO₂ NCs.

Samples	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield(%) ^c	LOI ^d
PAI	250	315	42	34.3
PAI/TiO ₂ NC (5 wt%)	252	320	60	41.5
PAI/TiO ₂ NC (10 wt%)	253	321	63	42.7
PAI/TiO ₂ NC (15 wt%)	254	321	65	43.5
PAI/TiO ₂ NC (20 wt%)	255	322	67	44.3

^aTemperature at which 5% weight loss was recorded by TGA. ^bTemperature at which 10% weight loss was recorded by TGA, ^cweight percentage of material left undecomposed after TGA analysis at a temperature of 800 °C under a nitrogen atmosphere. ^dLimiting oxygen index (LOI) evaluating char yield at 800 °C.

Figure 8: TGA thermograms of pure PAI and PAI/TiO₂ NCs under a nitrogen atmosphere at heating rate of 20 °C/min.

A small increase is observed for the residual weight of PAI NCs at temperatures above 600 °C. On the other hand, the char yield of pure PAI at 800 °C is 42%, whilst those of the NCs (PAI/TiO₂ NC 5, 10, 15, 20 wt%) at 800 °C are in the range of 60-67%. On the basis of LOI values (41-44), all macromolecules can be classified as self-extinguishing polymer NCs.

Optical study

UV-vis absorption has been utilized to illustrate the TiO₂ NPs disseminated within NCs matrix (Figure 9). It is recognized that TiO₂ is an oxide semiconductor and has an optical band gap of 385 nm. The mechanism of UV absorption in such materials includes the utilization of photon energy to stimulate electrons from the valence band to conduction band. It can be realized that all of the NCs have an absorption below the region of 400 nm (Figure 9). Figure 9 shows that the increase in TiO₂ NPs loadings leads to increased absorption percentage in UV wavelength region due to both nanofiller UV absorption and the light scattering. Consequently, the resulting PAI/TiO₂ NCs can block out the UV rays, but they are transparent to visible light.

CONCLUSIONS

To sum up, the PAI-TiO₂ NCs were fabricated by ultrasonic process. At first, an innovative thermally stable and optically active PAI matrix was prepared by direct step-growth polycondensation of 5-(2-benzimidazole)-1,3-phenylenediamine (4) with *N*-trimellitylimido-*L*-leucine (5) via TPP/TBAB as a condensing agent. Then TiO₂ NPs were modified with KH550 using ultrasonic irradiation to achieve suitable distribution of NPs within polymer matrix. FT-IR spectra and XRD studies reveal the existence of TiO₂ NPs in host polymer, while electron microscopic studies demonstrated that TiO₂

NPs were disseminated homogeneously on the well-known PAI matrix. TEM analysis presented loading of TiO₂ with average particle sizes about 25 nm in the polymer matrix. The PAI composites likewise demonstrated improved thermogravimetric stability, as compared with the PAI. According to the LOI values, the obtained NCs can be considered as self-extinguishing materials. It seems that the presence of natural amino acids in the PAI combined with bioactive TiO₂ NPs causes these NCs to be potentially bioactive. Based on our studies, PAI composites envisage the future development of biomimetic materials for the creation of a new bionanocomposite as a multicomponent and multifunctional material.

Figure 9: UV absorption spectra of the PAI and PAI/TiO₂ NCs with various TiO₂ contents.

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