



Photocatalytic polymerization of methyl methacrylate over neat and nitrogen doped anatase

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ABSTRACT

Nitrogen doped anatase was prepared by annealing TiO₂ (anatase form) powder in a stream of ammonia gas under heating at a constant heating rate for three hours with a constant flow rate of NH₃. Doping reaction was performed at 400°, 500°, and 600 °C. The modified titania was characterized by CHN, BET, XRD and UV-visible spectroscopy. It was found that doping nitrogen doesn't alter crystallinity of anatase as it was found from XRD patterns. Both Neat and nitrogen doped anatase used to initiate photocatalytic polymerization of methyl methacrylate (MMA) from an aqueous solution under irradiation with UV light from middle pressure mercury lamp. The resulted polymer was investigated by FTIR, NMR, SEM, TGA, XRD and GPC. The activity of reaction was calculated as a conversion percentage of monomer to the polymer against irradiation time. The photocatalytic activity of polymerization reaction falls in the following sequence anataseN500> anataseN400> anatase neat> anataseN600.

Keywords: TiO₂, N/TiO₂, nanocomposite materials, photocatalytic activity of titania.

INTRODUCTION

In photocatalytic polymerization, both composites of polymers and inorganic nanoparticles can be obtained. This type of polymer can be synthesized via mixing and *in-situ* polymerization. In the *in-situ* polymerization, the monomers are polymerized using organic initiators [1]. In photocatalytic polymerization, polymer formation is initiated by the excited nanoparticles by absorption radiation with sufficient energy ($h\nu \geq E_g$). When TiO₂ is irradiated with radiation of energy that is equal to or greater than band gap, produced conduction band electrons and valence band holes. These species then interact with monomer molecules producing polymer on the surface of the catalyst. Photocatalytic polymerization, not only offers a new application of semiconductor photocatalysis, but also provides a strategy to fabricate composites of polymers and inorganic nanoparticles[2]. Since the nanoparticles are retained during photocatalytic polymerization, polymers and the composites can be obtained simultaneously[3]. Photocatalytic polymerization offers a simplified process to prepare polymer/inorganic nanocomposites. This method has a promising future in fabricating photo-cured films, heterojunction composites, and protective coatings on semiconductors [3]. Considering that many modified band gap semiconductor nanoparticles are able to perform photocatalysis under UV and visible light irradiation such as TiO₂, ZnO and CdS, one can take advantage of solar energy to produce the nanocomposites[4]. Generally, these nanoparticle photocatalysts can initiate photopolymerization. According to band theory, semiconductors

have a completely filled valence band and empty conduction band at absolute zero. Irradiation particles of the photocatalyst produce conduction band electrons (e^-_{CB}) and valence band holes (h^+_{VB}). These species can diffuse through the solid followed by their trapping or recombination. A photocatalytic reaction is only efficient if electrons and holes are present on the surface in order to react with adsorbed species. Charge transfer from the bulk to the surface is possible only if it is thermodynamically allowed and has a sufficient lifetime [5].

The photogenerated electrons and holes upon irradiation of the photocatalyst can initiate polymerization, when reacting with adsorbed monomer molecules on the surface. This is distinguished from normal photopolymerization in which organic or inorganic photosensitizers are activated due to absorption of light with a sufficient energy to produce initiating free radicals[6,7]. In the last few years, composite materials have attracted considerable attention due to their interesting properties. Titanium dioxide has frequently been employed to prepare composites with these types of polymers. For instance, Wang and co-workers studied polymerization of MMA over titania under irradiation with UV light from mercury lamp. They reported formation two types of polymers, extracted and grafted polymer with titania surface[8]. In another study Hong and co-workers studied polymerization of MMA over ZnO. They reported formation a composite material of PMMA/ZnO[9]. Damm and co-workers studied photocatalytic polymerization of MMA over titania that was prepared by different methods. They found that activity of polymerization was affected by particle size and phase of titania[10]. In further study Damm and co-workers studied the photocatalytic polymerization of acrylate using iron doped TiO_2 . For this type of reaction, the photocatalytic initiation occurs upon irradiation with UV light.

MATERIALS AND METHODS

Surface modification : Doping nitrogen was performed by using 0.8 -1.0 g of anatase titanium (IV) oxide nanopowder, purity from supplier 99.7% anatase supplied by the Aldrich Company. The reaction was carried out by flowing ammonia under heating, the temperature ramp rate was $25^\circ C \text{ min}^{-1}$, and the ammonia flow rate employed was 92 mL min^{-1} . The reaction was run at the final temperature for three hours. Doping was undertaken at three different temperatures 400° , 500° and $600^\circ C$. After three hours, the NH_3 flow was stopped, and then samples were cooled to ambient temperature under a N_2 flow. The resultant modified materials ($TiO_{2-x}N_x$) were characterised with different spectroscopic and analytical methods such XRD, BET analysis and micro elemental analysis (CHN).

Photocatalytic polymerization : Photocatalytic polymerization was conducted over neat and nitrogen doped anatase at $400^\circ C$, $500^\circ C$ and $600^\circ C$. In each experiment, 150 mg of material was suspended in 100 mL of distilled water and to this 2 mL of MMA was added. The mixture then was stirred for ten minutes under a normal atmosphere prior to irradiation with UV light from a middle pressure mercury lamp (125 watt) with continuous stirring at $20^\circ C$ for two hours. The product then was separated by centrifugation, the solid then washed with water to remove unreacted monomer and then dried in a vacuum overnight. The crude product was then dissolved in THF with vigorous stirring and the resulted mixture was separated by centrifugation. The solid obtained was found to contain bound polymer and the liquid to contain extracted polymer. The formed polymer in the liquid was precipitated by adding an excess of methanol with stirring, then it was separated by filtration and derided in vacuum over night. Characterization of polymer was performed by using same methods that were used in case of polymerization over neat anatase such as FTIR, NMR, SEM, TGA and GPC.

RESULTS AND DISCUSSION

Parent and nitrogen doped titanium dioxide : Powder anatase samples treated in a flow of NH_3 at $400^\circ C$, $500^\circ C$ and $600^\circ C$ are denoted as titaniaN400, titaniaN500 and titaniaN600 respectively. The nitrogen and hydrogen contents of the parent and nitrogen doped samples were determined by elemental analysis

and the data are presented in table 1. From this data, it can be seen that ammonia is effective for the introduction of nitrogen into the samples, as expected from the yellow colouration of the samples that was observed to develop upon NH_3 treatment. Furthermore, the level of nitrogen dopant increases and is substantial after treatment at 600°C . In addition, hydrogen is observed to be present in nearly all samples. BET surface areas have been measured for the three sets of samples and the results are presented in table 1, where it can be seen that the surface area of the anatase materials is roughly constant upon NH_3 treatment for the 400 and 500°C samples. It appears that the surface area is slightly enhanced upon NH_3 treatment. In all cases, powder XRD indicates the retention of the original crystal phase upon reaction. The UV-visible diffuse reflection spectra of doped and undoped samples are shown in Figure-1. For all doped samples, there are considerable shifts of the absorption shoulders into the visible light region. The absorption shoulder in the range 400- 550 nm is related with the presence of doped nitrogen with these samples and it increased with increasing in nitrogen content. Additionally, these samples after they have been doped, were pale- yellow in colour [11,12] and the colour deepened gradually with elevation in doping temperature.

It has been reported that the colour of the N doping samples partially results from bulk reduction. This probably arises from existence of mixed $\text{N}2\text{p}$ states with $\text{O}2\text{p}$ states or isolated $\text{N}2\text{p}$ states lying above valence band [13,14]. The presence of the visible absorption band in the electronic spectra figure 1 for the doped samples provides a possible indication that nitrogen may has changed the electronic structure of titania effectively [15]. Normal absorption in titania is due to an electronic transition from the valance band to the conduction band which commonly occurs in the ultraviolet region of the spectrum [16,17].

Table 1. Elemental analysis for doped TiO_2 measured by CHN micro elemental analysis.

Catalyst	H wt% \pm 0.03%	N wt% \pm 0.02%	N/H atomic ratio	BET surface area (m^2/g) \pm 1	Particle size (nm) from XRD
anatase parent	0.31	0.00	-----	112	16.5
anataseN400	0.28	0.35	0.09	113	16.1
anataseN500	0.24	0.48	0.14	116	15.6
anataseN600	0.21	1.80	0.61	89	17.1

These results showed that the ratio of nitrogen content for the nitrogen doped titania samples was increased with increase in the doping temperatures. Additionally, from the stoichiometric values for atomic ratio of H/N for the doped nitrogen species, it can be seen that the expected doping species don't correspond simply to NH_3 and NH_2 residues.

UV- Vis spectra for nitrogen doped anatase:

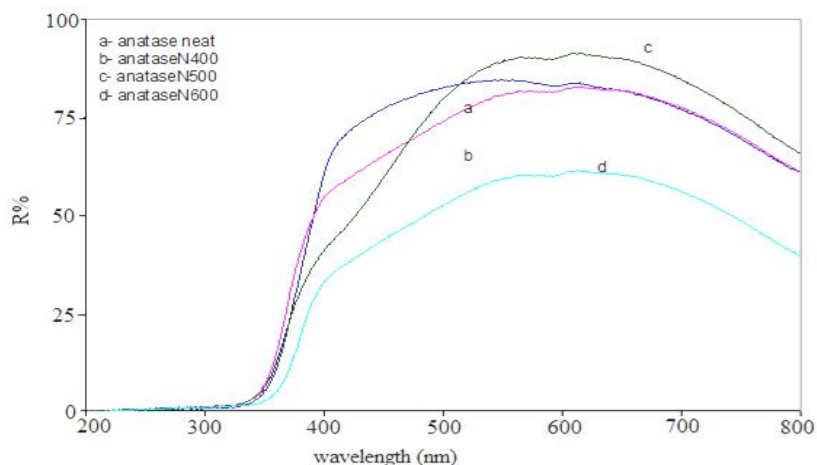


Figure 1. UV-visible diffuse reflection spectra for neat and nitrogen doped anatase

The UV-visible diffuse reflection spectra were measured for parent and doped forms of TiO_2 . These spectra are shown in figure 1. From these results, it was observed that, there is red shift in the band edge absorption of the doped samples ($\text{TiO}_{2-x}\text{N}_x$). This means that, the photoresponse of these samples was shifted towards the visible region of the spectrum. It was reported that nitrogen could be loaded in the lattice of titania. Generally, the extension of the absorption spectrum from UV light to the visible range arises from contribution of both doped nitrogen atoms and oxygen vacancies in the lattice of TiO_2 . That is because the interstitial nitrogen atoms would induce the local states near the valence band edge and the oxygen vacancies generate local states below the conduction edge [18]. Generally, doped nitrogen atoms induce local states close to the valence band, while oxygen vacancies induce local states below the conduction band. These local states can enhance light harvesting for the catalyst in both the near UV and visible region of the spectrum. Oxygen vacancies induced by doping TiO_2 can act as colour centres. The electrons that leave oxygen vacancies may interact with the adjacent Ti(IV) species to generate Ti(III) species as colour centres. The presence of these colour centres in titania can increase the absorption of visible light for the N doped titania [19].

XRD patterns for parent and doped TiO_2 Samples: In all cases, powder XRD indicates the maintenance of the original crystal phase upon reaction. Generally, specific surface area is mainly independent of the amount of doped nitrogen. The XRD patterns for the doped and undoped samples are similar, and their patterns did not differ significantly except for slight variation in the intensity and broadening of their peaks. Generally, samples that doped at 400° and 500°C were relatively broader than that doped at 600°C . The Scherrer equation[20] was used in the estimation of the particle size for neat and doped samples. When the size of crystallites is less than 100 nm, appreciable broadening of the x-ray diffraction reflections occurs. This may be related to the actual size of the crystallites, in this case the observed line broadening can be used in the estimation of the average particle size. For application for this equation, the following assumptions must be made: negligible broadening caused by the instrument, negligible broadening due to strain disorder and when working from a single reflection coherent diffraction domain size is isotropic. In the simplest case where the particles are free from strain, the size of the particle can be estimated from a single diffraction peak. XRD patterns for neat and doped samples are shown in figure 2.

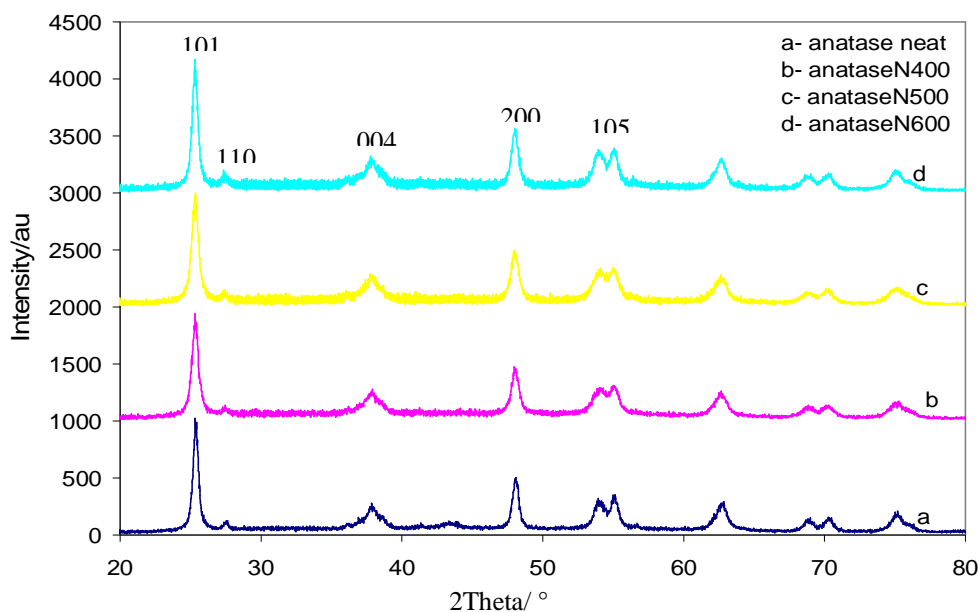


Figure 2: XRD patterns for neat and nitrogen doped anatase.

The XRD patterns for neat and doped samples of anatase are shown in Figure-2. These samples possess similar diffraction peaks without significant changes in the positions of these peaks occurring after doping [21]. In addition, doping anatase at 600 °C gives slightly higher intensity with sharper peaks, which indicates that well crystallized materials with a relatively large particle size can be produced at 600 °C by nitrogen doping. For the doped samples, there is not evidence for the occurrence of any phase transformation. For neat anatase and that doped with nitrogen, there is a residual peak around ($2\theta = 27$) which arises probably for rutile phase. It has been reported that, when replacing O^{2-} in titania by nitrogen species by doping minimal structure change occurs, although the radius of the nitrogen ion (0.171nm) is larger than that for the oxygen ion (0.132nm) [22]. Hence, the expected change in the structure due to doping nitrogen in this range of concentrations would be relatively minor [23].

Photocatalytic polymerization over neat anatase: Excitation of titania particles by absorption of light of a suitable energy ($h\nu \geq E_g$) leads to production of conduction band electrons and valence band holes, which can be used for photocatalytic polymerization when reactions with monomer molecules occur[24]. Radical species due to reaction of monomer molecules with h^+_{VB} yields primary radicals which participate in polymerization reactions[25]. To investigate photocatalytic polymerization over neat anatase a series of experiments were undertaken at different reaction conditions using MMA as a monomer in an aqueous suspension of titania under irradiation with UV light from a middle pressure mercury lamp (125 Watt). Different parameters were investigated.

Characterisation of the polymer: Polymer formation was characterized by using FTIR spectroscopy, NMR spectroscopy, GPC, SEM and TGA analysis for the bound and extracted polymer. The FTIR spectra for PMMA extracted and PMMA grafted anatase are shown in Figures-3a and 3b.

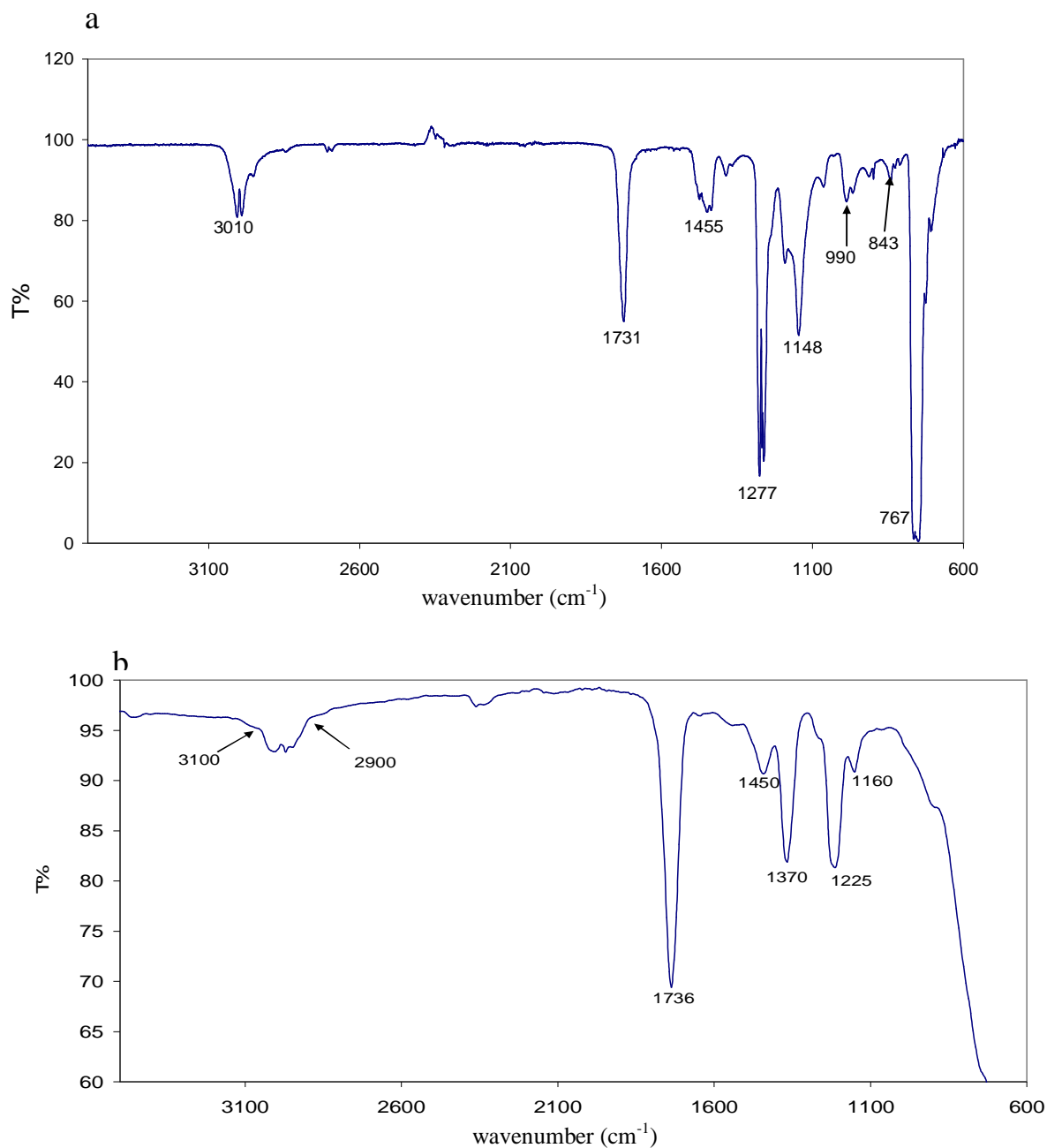


Figure 3. The FTIR spectra for PMMA extracted (a) and PMMA grafted anatase (b)

Extracted and grafted PMMA on the anatase show a characteristic sharp band at 1730-1736 cm⁻¹. This sharp peak indicates the presence of the grafted PMMA on the anatase and the formation of the PMMA/anatase composite. For the extracted PMMA, the broad band around 3010 cm⁻¹ is related to free CH₃ vibrations in the PMMA. The band at 1000-1460 cm⁻¹ can be assigned to the C-O-C stretching mode of ester bond in PMMA. The other bands at 750-950 cm⁻¹ are due to the bending of C-H bonds [25]. For PMMA grafted anatase, the broad band at 2900-3100 cm⁻¹ is due to the stretching vibrations of -OH groups on the titania surface. In addition, the FTIR spectrum of PMMA grafted anatase shows another characteristic peaks at 1450, 1370, 1225 and 1160 cm⁻¹. These are assigned to the C-H, -CH₂ and C-O-C band of PMMA. It seems that the CH₃ vibration mode for PMMA grafted anatase at 3000-3100 cm⁻¹ overlaps with the stretching vibration of OH group [26]. Generally, this type of polymerization requires

adsorption of monomer molecules on the surface of solid catalyst and then the solid particles are excited by absorption radiation energy.

^1H NMR spectroscopy: Further investigation for the extracted polymer from composite materials of PMMA/ anatase was undertaken by measuring ^1H NMR spectra for MMA and extracted PMMA as shown in Figures-4 and 5.

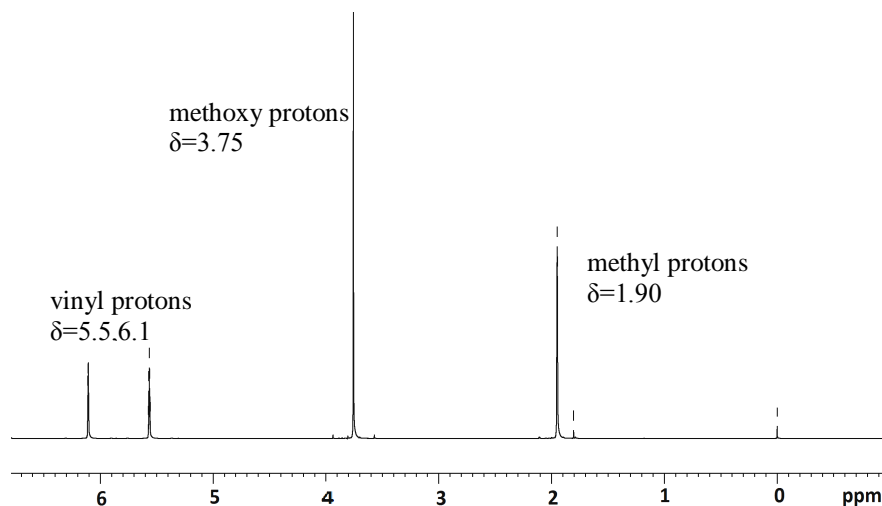


Figure 4. ^1H NMR spectrum for MMA in CDCl_3 .

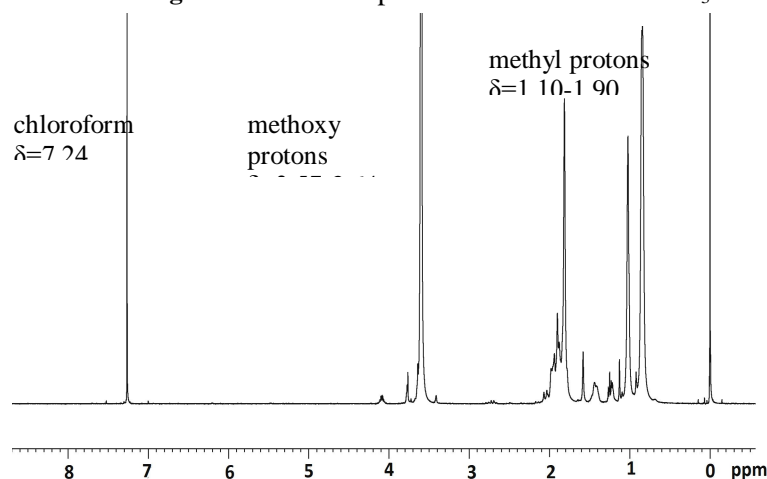


Figure 5. ^1H NMR spectrum for the extracted PMMA in CDCl_3 . This type of polymer was extracted from titania using THF and then it was precipitated with an excess of methanol

The most interested thing in these spectra is that the peaks at $\delta = 5.5$, and 6.0 which are assigned to the $(\text{H}_2\text{C}=\text{C}-\text{CH}_3)-$ in MMA (Figure- 4) are completely absent in extracted PMMA as shown in Figure-5. The main features of ^1H NMR spectrum for the extracted PMMA, is the presence of a peak which corresponds to the methoxy protons at $\delta = 3.57$ - 3.64 [27]. It is observed that, the extracted PMMA was similar to PMMA that is synthesized by normal chemical polymerization.

Scanning electron microscopy (SEM) : Morphological studies for each of neat anatase, grafted with PMMA, extracted PMMA have been undertaken using Scanning Electron Microscopy (SEM), and the resultant micrographs are shown in the Figure-6.

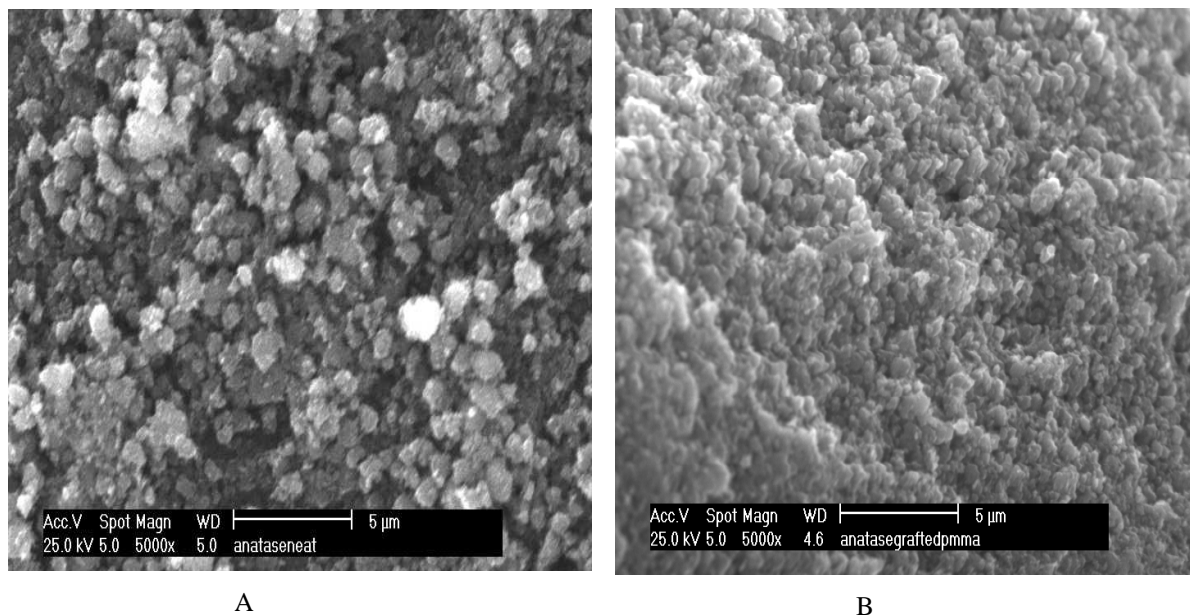


Figure 6. SEM images for (A) neat anatase and (B) grafted anatase with PMMA.

From these figures, the change in the morphology of the surface after grafting with the polymer can be seen. PMMA grafted anatase exhibited high dispersion on the surface and anatase nanoparticles are aggregated severely after grafting with PMMA. That may result from a high surface energy when PMMA was grafted on the surface [28].

Thermal gravimetric analysis (TGA): The grafted polymer was further investigated by thermal gravimetric analysis TGA that was performed under both air and nitrogen atmospheres and the identical data was obtained for the different atmospheres. From this data, there is an evidence for the formation of the grafted polymer on anatase due to the characteristic mass loss about 12% in the 300- 500 °C temperature range. The most important point here is that polymer-grafted anatase begins to decompose at different temperature than that for the traditional PMMA (extracted polymer). This is interpreted as resulting from the interaction between polymer chains and anatase nanoparticles^(29,30). This interaction occurs between Ti^{4+} and TiOH surface species with electron donating atoms in PMMA (oxygen atoms). TGA for the composite anatase/PMMA in air is shown in figure 7.

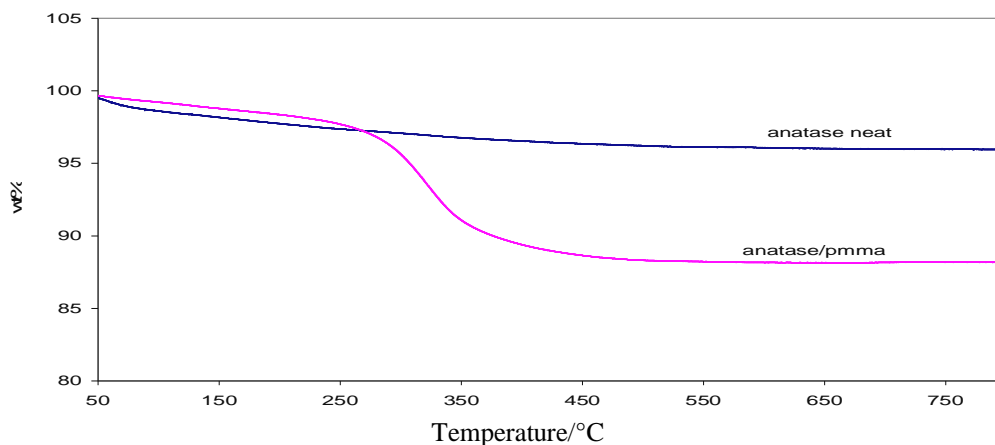


Figure 7. TGA for neat and grafted anatase with PMMA in air. From TGA result, the conversion percentage of grafting 13.6%.

Optimization weight of the TiO₂ used : In order to find the optimal weight of anatase photocatalyst, a series of experiments was performed using different masses of the catalyst with the reaction mixture containing 2 mL of purified MMA. Experiments were carried out at 20 °C in air with irradiation for two hours. These results were repeated three times in the range of 0.001 to 0.300 g, and the average of the results are plotted in figure 8, the average error bar for the results was $\pm 0.25\%$. From these results, it was found that 0.15 g of TiO₂ is the optimum weight for this system. The experiments of using different loading of titania have shown a considerable variation in product formation. Initially there was increase in conversion percentage with increase of used titania weight. After this weight, any increase in titania amount doesn't increase reaction rate significantly. After this step, using higher weight of titania results in reduction rate of reaction. According to these results, there is an optimal weight of anatase, which should be used to give the best photocatalytic activity. In this system, the optimal weight is 150 mg 100 mL⁻¹. Lower weights than this give a direct proportionality between weight and photocatalytic activity. Using higher weights leads to negative results in comparison with the optimum weight of titania. The explanation for this is that when using a low mass suspension of anatase the number of titania particles are few in comparison with the number of the incident photons that reach into the reaction mixture [31]. According to the second law of photochemistry, each atom or molecule absorbs one photon. So that, the absorbed photons will be few, this gives a direct proportionality between the used weight and photocatalytic activity. For more dense suspensions of anatase (more than 150 mg), the particles form an inner filter which absorbs a high proportion of the incident photons and scatters the other part of the light, leading to a reduced number of active photons for the reaction. Therefore, it is necessary to find a determined weight of titania which absorbs a high portion of the incident photons [31].

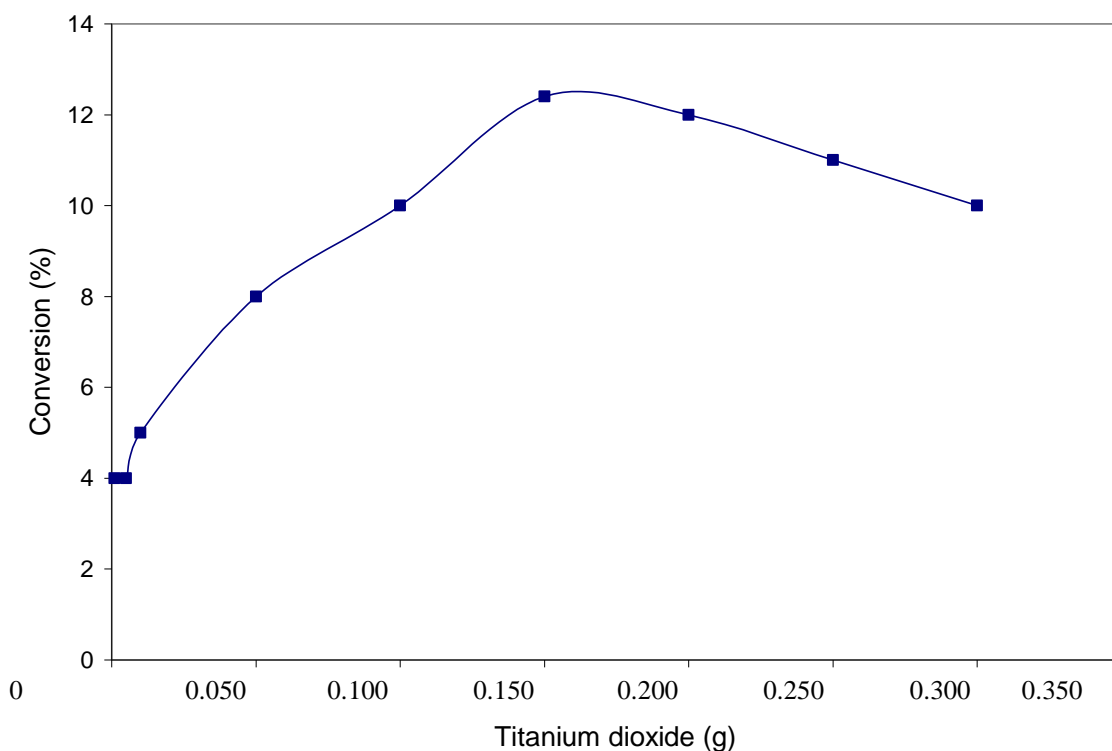


Figure 8: Optimization weight for the photocatalytic polymerization over TiO₂, the average error bar for these results $\pm 0.25\%$

Effect of exposure time : The effect of radiation exposure time was studied using 0.150 g of anatase suspended in 100 mL of distilled water containing 2 mL of purified MMA under air for various durations at 20 °C. The results were repeated twice for a period from 30 to 210 minutes.

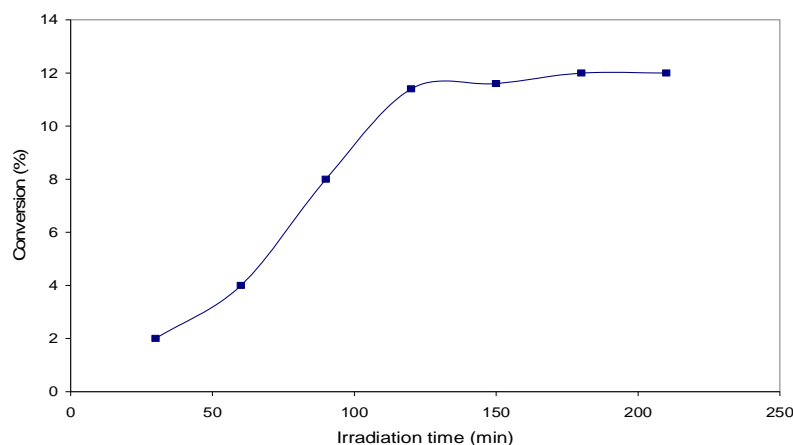


Figure 9. Effect of time exposure on the photocatalytic polymerization of MMA over TiO₂.

The average error bar was $\pm 0.30\%$, and the average results are shown in Figure -9. From this study, it can be seen that there is progressive increase in conversion of monomer into polymer with the time of reaction and keeping other reaction conditions constant. The conversion percentage was increased from initial stage of polymerization until up to two hours of exposure. After this point, there was no significant increase in the conversion percentage. Initial increase in conversion with exposure time is probably due to formation more radicals that contribute to polymer formation. After higher exposure time (more than two hours), there was no significant increase in conversion with the time. That is may be due to termination of growing grafted chains with the newly formed primary radicals on the surface of titania.

Effect of the amount of the used monomer : To investigate effect of the amount of the used monomer for this system, different amounts of MMA from 0.25 to 3.00 mL were used with 0.15 g of anatase in 100 mL of distilled water and irradiation under air for two hours at 20 °C. The average error bar was $\pm 0.21\%$, the results are shown in Figure-10.

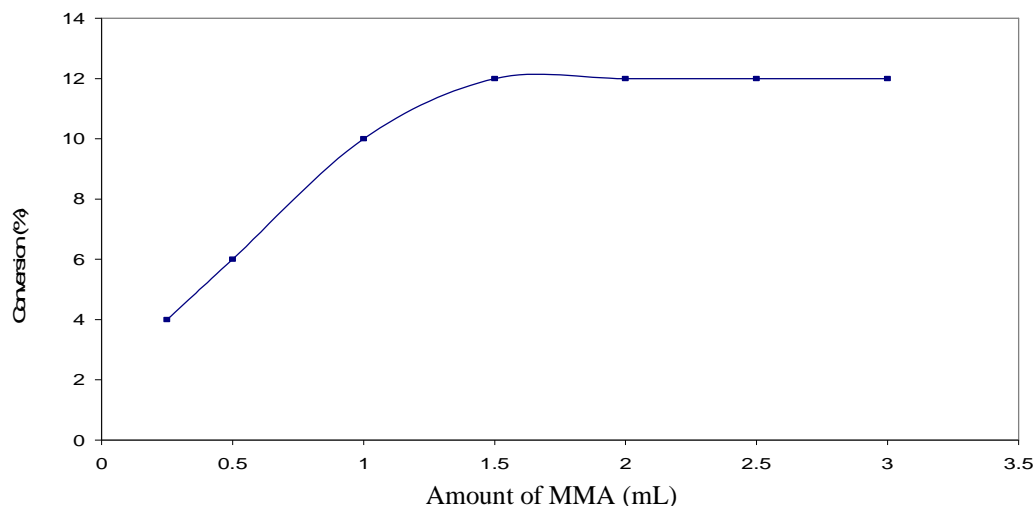


Figure -10: Effect of the amount of MMA on photocatalytic polymerization over TiO₂.

When using small amounts of the used monomer initially, it is clear that the rate of reaction was progressively increased but beyond a certain point, conversion was constant. In this type of reaction, the rate of reaction doesn't depend mainly on the concentration of the reactants, but it depends on the surface of the catalyst. Initially, the small amount of MMA would adsorb on the surface and participate in the reaction progressively with the increase for MMA until a certain point. Beyond this point, any further increase amount of MMA becomes ineffective on the rate of reaction.

Effect of temperature on the reaction: The effect of the temperature on the photocatalytic polymerization was carried out by following the conversion of MMA into PMMA at different temperatures with all of the other parameters of the reaction being fixed at 2 mL MMA, 0.15 g of anatase with 100 mL of distilled water and irradiation for two hours in air. The results showed enhancement in the rate of reaction with increasing temperature. The error bar was $\pm 0.42\%$, These results are shown in Figure-11.

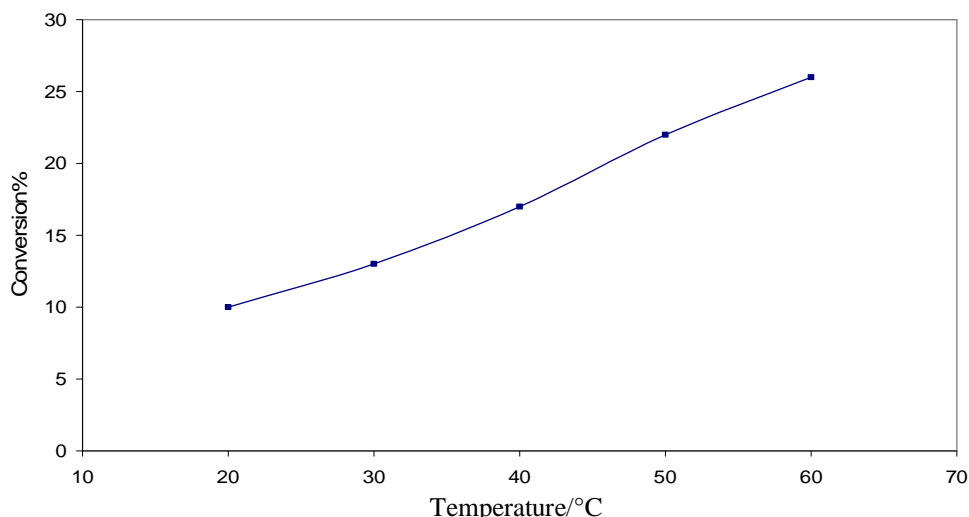


Figure 11. Effect of temperature on the photocatalytic polymerization.

From these results, it can be seen that, increase temperature of reaction in this range results in an increase of rate of reaction. This probably arises from effect of temperature on the adsorption and desorption processes on the surface. However, photoreactions are not very sensitive toward minor changes in the temperature [32]. However, some reaction steps are potentially dependent on temperature such as adsorption and desorption. Generally, an increase in the rate of reaction with an increase of the temperature may be attributed to the effect of temperature on these steps on the TiO_2 surface [33]. These steps involve adsorption of monomer molecules on the surface of titania, then producing active radicals due to reaction of monomer molecules with electron/ hole pair.

Activation energy for photocatalytic polymerization over titania : The activation energy for the photocatalytic polymerization reaction can be determined by applying the Arrhenius equation after measuring rate of the reaction at least three temperatures, and rate constant can then be calculated from the relation between rate of the reaction and initial concentration of MMA[34]. Then by plotting $1/T$ on the x-axis and $\ln(k)$ on the y-axis, the gradient can be used to find the activation energy as shown in Figure-12.

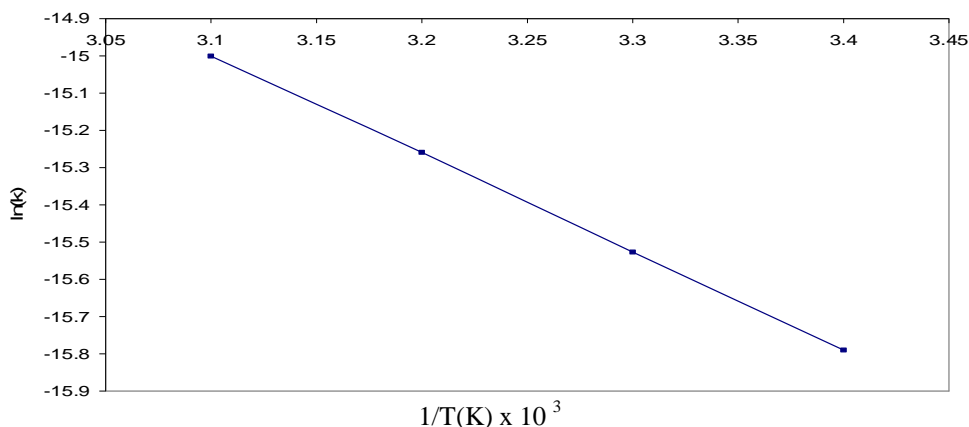


Figure 12: Arrhenius plot for the photocatalytic polymerization over anatase.

From plot, gradient = -2630 K^{-1} , $-E = \text{gradient} \times R = -2630 \times 8.31 = 21865.82 \text{ J mol}^{-1}$, $E = 21.87 \text{ kJ mol}^{-1}$

Generally, photoreactions are not too sensitive towards minor variation in temperature. The steps that are potentially dependent on reaction temperature such as adsorption and desorption are not the rate determining steps in this type of reaction. However, this value of activation energy is similar to that found in the other photocatalytic reactions over titania such as photocatalytic oxidation of alcohols over TiO_2 [35,36]. However, this amount of activation energy is higher than that required to transfer electron from valence band to the conduction band (3.20 eV). This amount of activation energy is probably related to adsorption/desorption processes on the surface.

Effect using Et_3N on the photocatalytic polymerization: To investigate effect of addition of an electron donor on the photocatalytic polymerization of MMA, 2mL of MMA was suspended with 0.15 g of anatase with mixing and irradiation for two hours at 20°C under normal atmosphere with using various amounts of triethylamine additive (Et_3N). The average error bar was $\pm 0.34\%$, and these results are shown in Figure-13.

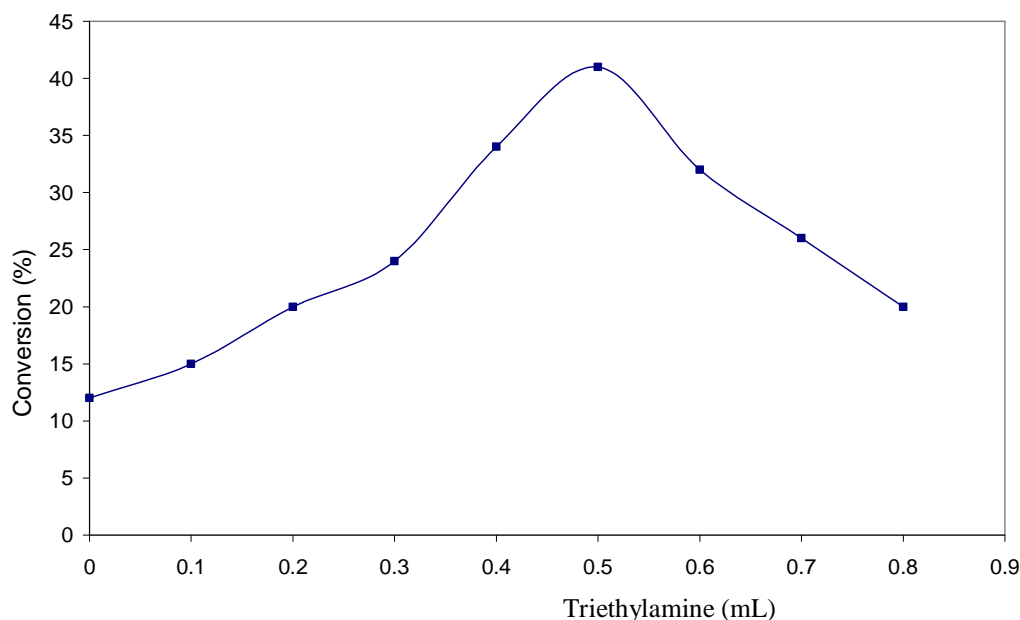


Figure 13. Effect of using Et_3N on the photocatalytic polymerization.

From these results, a maximum conversion of around 41% was obtained using 0.5 mL of Et₃N. This result is probably due to facile formation of the radicals on the surface of anatase with the presence of Et₃N. Beyond this volume of Et₃N the conversion was reduced. That is expected as polymerization in this case becomes controlled by initiation with Et₃N mainly. Initiation with Et₃N would be expected to be less effective in photocatalytic polymerization [37].

The number averaged molecular weights (M_n) for the extracted PMMA when use anatase and anatase/Et₃N were 62,000 and 35,000 respectively. From these results, using anatase alone affords a higher molecular weight, while using anatase/ Et₃N gives lower molecular weight and higher conversion percentage. These observations are probably due to the relation between rate of polymerization and the viscosity of polymerization mixture [38]. High viscosity would give low rate of polymerization (low conversion percentage), while low viscosity would give high rate of polymerization (high conversion percentage). At high viscosities, the chain growth propagation reactions and chain termination reactions become diffusion controlled [38].

Photocatalytic polymerization over nitrogen doped anatase: To investigate the effect of doped nitrogen in photocatalytic polymerisation of MMA, a series of experiments were undertaken. In each one, 0.150 g of doped anatase suspended in 100 mL of distilled water with 2 mL of MMA under air for a durations of two hours at 20 ° C. The average error bar was $\pm 0.28\%$, the results are shown in Figure-14.

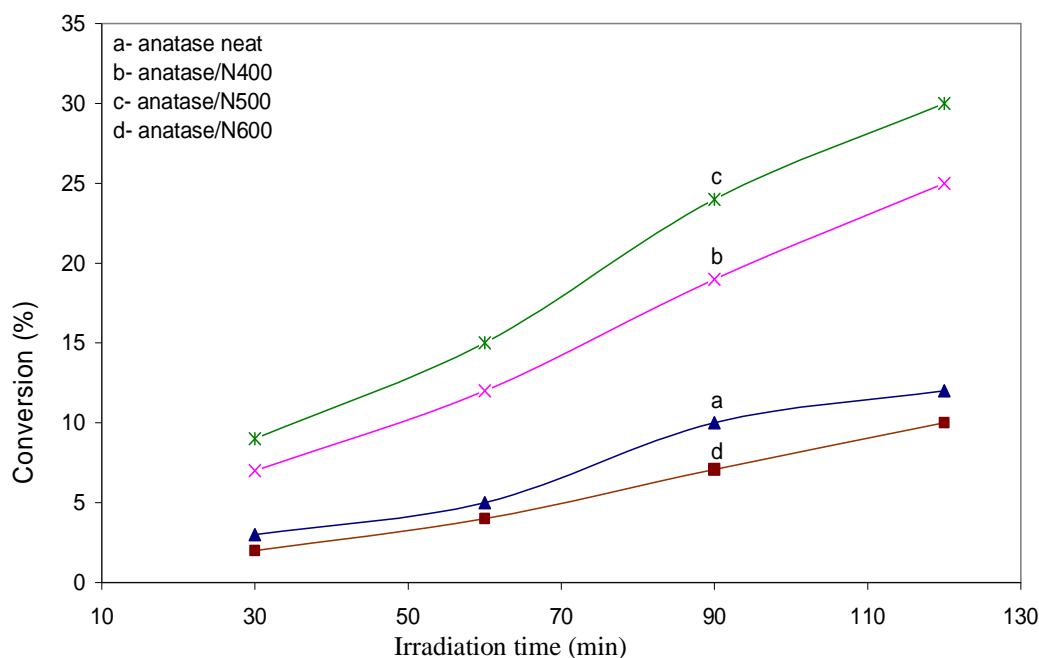


Figure 14. Photocatalytic polymerization over anatase doped with nitrogen.

From these results, it can be seen that there is enhancement in the photocatalytic activity for the doped samples, anataseN500 and anataseN400 that gives relatively higher conversion percentage for the formation of PMMA over these catalyst in comparison with the neat anatase under the same conditions. Generally, the activity for the photocatalytic polymerization for these catalysts fall in the order: anataseN500> anataseN400> anatase neat> anataseN600. The improvement in photocatalytic activity for these samples, as mentioned previously, probably arises from the increase in the absorption intensity in the near UV region with the increase in nitrogen content. Additionally, these samples have a relatively higher surface area with smaller particle size and the decrease in particle size with the increase in surface area produces a higher photocatalytic activity [18]. In contrast, anataseN600 exhibits a lower photocatalytic activity in comparison with neat anatase. In this sample, that has higher nitrogen content and a greyish

green colour, the high nitrogen content may assist in formation of recombination centres close to the valence band of the catalyst. These recombination centres can increase rate of recombination leading to reduction photocatalytic activity [34]. The number averaged molecular weights (M_n) for the extracted PMMA for anatase neat, anataseN400, anataseN500, and anataseN600 were 62,000, 55,000, 52,000, and 63,000 respectively. From these results, the highest molecular weight was obtained with a lower conversion percentage, while a lower molecular weight was obtained with a higher conversion percentage. This may be as a consequence of the relation between rate of the polymerization reaction and the viscosity of the polymerization mixture [33]. High viscosity would result in a low rate of polymerization (low conversion percentage), while low viscosity would result in a high rate of polymerization (high conversion percentage). At high viscosities, the chain growth propagation reactions and chain termination reactions become diffusion controlled [38].

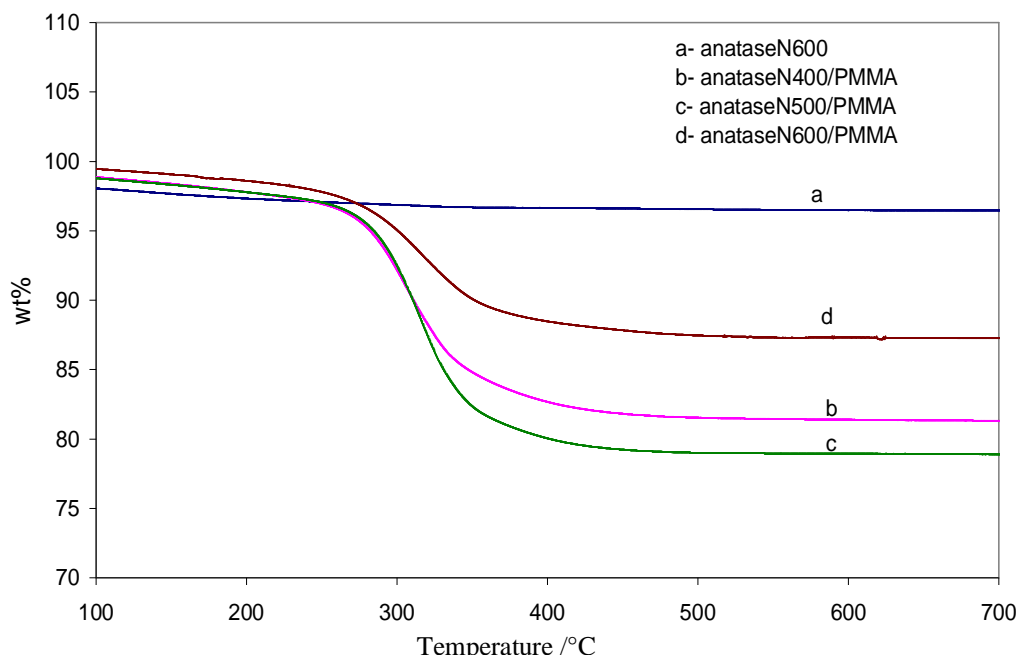


Figure 15. TGA for PMMA grafted nitrogen doped anatase.

From the above results, there is an evidence for the formation of the grafted polymer over anatase due to a characteristic mass loss about 12- 23% of the weight in the temperature range of 300- 500 ° C. In addition to that, and as was mentioned earlier, the polymer grafted titania (PMMA/anatase) begins to decompose at different temperature than that for the traditional PMMA (extracted polymer). This is probably due to interaction between polymer chains and the surface of anatase nanoparticles[39]. In addition to that, the higher percentage mass loss can be seen with anataseN500, while the lowest percentage loss occurs with anataseN600. So that the grafting percentage follows the order: anataseN500> anataseN400> anataseN600, and the grafting percentage for these samples were 25%, 22% and 12% respectively.

APPLICATIONS

The results are useful to know the photocatalytic activity of titania and doped titania.

CONCLUSIONS

In this study, doping titanium dioxide with nitrogen was performed at three different temperatures, 400 °C, 500 °C and 600 °C. It is believed that doped nitrogen species within titania may exist as interstitial species

or substitutional species or a combination of both these states. It was found that doping titania with nitrogen doesn't alter its structure, as the XRD patterns for the doped samples were similar to those of the non-doped counterparts. In addition, doping titania with nitrogen generates a red shift in its absorption spectrum, possibly as a result of mixing of 2p states of the doped nitrogen species with the O 2p states as suggested in the literature. Doping samples at 400 °C and 500 °C results in higher BET specific surface areas. The photocatalytic activity for the various samples was investigated by photocatalytic polymerization of methyl methacrylate was undertaken for selected titania samples. It was found that, doping titania at 400 °C and 500 °C resulted a higher photocatalytic activity in comparison with parent undoped titania, while doped samples at 600 °C showed lower photocatalytic activity. The improvement in photocatalytic activity for titaniaN400 and titaniaN500 probably arises from the increase in the absorption intensity in the near UV and visible region with increase in nitrogen content.

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