Synthesis and evaluation of photoactive polyethylene terephthalate-*g*-ethylmethacrylate based on waste PET

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ABSTRACT

Waste polyethylene terephthalate (PET) was grafted with ethyl methacrylate monomer (EMA) using potassium persulphate; (KPS) as initiator in absence/ presence of anatase and N-doped titanium dioxide; (TiO_2 and N-doped TiO_2) to produce a photoactive grafted copolymer that can be used in water treatment. Effect of various concentrations of monomer and initiator on grafting yield (G%) and grafting efficiency (GE%) were investigated. The effect of added TiO_2 and N-doped TiO_2 during grafting of waste PET on the photocatalytic activity of the resulting copolymer was also investigated. FTIR, TGA and SEM techniques were employed to characterize the prepared samples. Results revealed that optimum G% and GE% were obtained upon applying monomer and initiator concentrations of 2×10^{-3} and 1.5×10^{-3} mol/L at 70 °C after 300 minutes. The photocatalytic activity of the prepared grafted PET copolymer was evaluated by investigating the degradation of methylene blue dye using the grafted copolymer as photocatalyst. The results showed that the grafted PET containing N-doped TiO_2 gave the highest rate of photocatalytic degradation of methylene blue using solar energy as a source of irradiation.   © 2013 Trade Science Inc. - INDIA

INTRODUCTION

Consumed polyethylene terephthalate (PET) products became one of the environmental problems. (PET) is extensively used polyester in producing bottles and containers. Besides, it participates in manufacturing automobiles products, sporting goods, house-wares, lighting products and power tools[1]. The increment in beverage consumption and the substitution of glass by polyethylene terephthalate (PET) in the production of bottles led to a globally growing concern for the post consum-ing disposal of PET bottles to enhance the waste management[2]. Normally, PET is a non degradable plastic as there is no specific organism that can consume its molecules. Degrading PET biologically is so complicated and expensive[3]. Polyethylene terephthalate (PET) is considered as a widely used thermoplastic polyester in various applications as diverse as textile fibres, films, bottles and other molded products[4]. The majority of the world PET production is for synthetic fibers (with bottle production accounting for around less than half of global demand. One of the main reasons for the wide-

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spread use of PET is their possibility of producing a number of different grades over a broad range of different molecular weights products[5]. Waste PET; either film or fiber can participate in copolymerization with various monomers[6-8]. The increment in environmental and economical values of the PET recycling industry induces a cosmopolitan interest. However, the use of recycled PET in many applications is limited due to lack of some desirable properties[9]. To overcome this disadvantage, the consumed PET; could be grafted or surface coverage. The grafting process is considered as a convenient alternative for reusing discarded PET. It is assumed to be beneficial processing for the modification of a polymer surface such as treatment by plasma, electron beam radiation and UV-light-induced grafting[10,11]. Among these treatment methods for the surface modification of polymers, the photo-induced UV grafting onto polymer surfaces is a generating method to attain desired properties for specific uses. UV grafting is an attractive way to impart various functional groups to a polymer. This allows some changes in surface characteristics without causing serious modifications to the mechanical properties of the polymer matrix[12,13].

Gamma radiation is used to induce graft copolymerization of plastic and rubber substrates[14,15]. Polyethylene terephthalate (PET) film was grafted by acrylic acid (AA) and n-butyl acrylate (BA) in the presence of gamma radiation effect to induce the grafting process. The results showed that the grafted films have strong and stable antibacterial activities for PET/AA films. The performance of PET fabric was improved by using photo-induced surface grafting with glycidyl methacrylate (GMA) as monomer[16]. Ethyl methacarylate (EMA) is one of the employed monomers in grafting processes for natural and synthetic polymers. Carboxymethyl cellulose and chitosan were grafted by acrylonitrile, methyl acrylate, ethyl acrylate and ethyl methacrylate. Although the reaction conditions were analogous, the rate of grafting was different. This was due to the propagation by radicals formed on the backbone polymer[17-19]. Atom transfer radical polymerization was utilized to graft ethyl methacrylate onto polystyrene in several formulations. The controlled growth of the side chain afforded the graft copolymers with various polydispersities[20]. Graft co-

polymers of ethyl methacrylate on waxy maize starch and hydroxypropyl starch were prepared via free radical polymerization. This led to more amorphous materials with larger particle size having lower apparent density and water content than carbohydrates[21]. Grafting polymerization of ethyl acrylate and methyl methacrylate onto cellulose chains exhibited an attempt of restoration for both artificially and naturally aged paper based materials. The presence of fillers in the raw materials decreased the grafting yields[22].

Photocatalysis with semiconductors have recently emerged as an advanced oxidation process for environmental decontamination. Titanium dioxide (TiO_2) can be considered among the most promising compounds for photocatalysis applications. TiO_2 is stable in aqueous media and tolerant to both acidic and alkaline solutions. It is inexpensive, recyclable, reusable and relatively simple to produce. Furthermore, its redox potential is appropriate to initiate a variety of organic reactions. The large band gap of TiO_2 lies in the UV range, which allows for only 5–8% of sunlight to be useful for the activation of the catalyst. Therefore, a visible light activated catalyst is desired. It can take the advantage of a larger fraction of the solar spectrum and would be much more effective in environmental cleanup. Substitutional doping to TiO_2 has revealed an improvement in ultra violet and visible light photocatalytic activity[23-25]. N-doped TiO_2 shows a significant shift of the absorption edge to a lower energy in the visible light region[26].

In the present investigation, waste PET was grafted by EMA (PET-*g*-EMA) in presence/absence of TiO_2 as a photocatalyst. The effect of introducing of TiO_2 and N-doped TiO_2 during grafting process of waste PET on the photocatalytic activity of the grafted polymer was studied. The prepared grafted samples were characterized using FTIR, TGA and SEM techniques.

EXPERIMENTAL

Materials

Waste PET was obtained from consumed PET soft drink bottles, in Cairo, Egypt. Labels and caps were removed from the bottles then cleaned, dried and chopped, pressed at 260 °C into flakes. They were cut

into quadrilateral pieces. Ethyl methacrylate (EMA), potassium persulphate (KPS) and TiO_2 anatase were supplied from Sigma Aldrich Company. The nitrogen doped TiO_2 (Kronos vlp 7000), a commercially available visible light activated TiO_2 photocatalyst (Kronos International Inc., D-51373) was used in this study. All solvents were purified before being used.

Instruments

Infrared (IR) spectra were obtained on a JASCO FT/IR-6100 FT-IR spectrometer with JASCO ATR PRO410-S.

TGA analysis, from Perkin-Elmer (TGA7) was employed; as the samples were encapsulated in aluminum pans and heated under nitrogen atmosphere with a heating rate of 10 °C/min, ranging from room temperature up to 600 °C.

SEM (JXA-840A, JEOL) scanning electron microscopy (SEM) was used at a voltage of 30 kV for investigating the freeze-fractured samples immersed in liquid nitrogen. They were then coated with thin layers of gold.

Grafting process

Weighed samples (200 mg) of PET flakes were dipped into a 100 mL polymerization tube containing a known concentration of EMA (0.5×10^{-3} - 3×10^{-3} mol/L) in 20 mL of distilled water. The tube was placed in an oil bath adjusted to the polymerization temperature, and nitrogen gas was allowed to pass through the solution for 30 minutes. Various concentrations of potassium persulphate; KPS, as initiator (0.5×10^{-3} - 2×10^{-3} mol/L) were dissolved in distilled water, added portion wisely to the grafting flask to initiate the graft copolymerization process under nitrogen atmosphere with continuous stirring for a predetermined temperature and time. At the end of the polymerization time, the PET samples were removed from the polymerization tube and subjected to soxhlet- extraction for 6 h with methanol and distilled water respectively. The grafted samples (PET-*g*-EMA) were dried in an air oven at 60 °C till constant weight. The grafting process was carried out in absence/presence of TiO_2 and N-doped TiO_2 in concentrations of 0.01 and 0.05 g/L. The grafting parameters were calculated according to the following equations[27]:

Grafting yield (G%) = [(W₁ - Wₒ) / Wₒ] x 100

Grafting efficiency (GE%) = [(W₁ – Wₒ) / (W₂ – Wₒ)] x 100

Homopolymer (H%) = [(W₂ - W₁) / W₃] x 100

where W_o and W_1 are the weights of the initial and grafted matrix (i.e., weight of grafted product after extraction), respectively, W_2 the crude product before extraction, and W_3 the weight of monomer.

Photocatalytic reactions

Photocatalytic reactions were carried out using a solar photoreactor with ten fluorescent lamps generating approximately 120 Wm^{-2} of wavelength ranging from 400 - 700 nm. The prepared grafted polymer inserted in a solution containing methylene blue was allowed to equilibrate for 30 min in the darkness, and then it was irradiated under sunlight illumination. During these treatments, the suspensions were magnetically stirred. The photocatalytic efficiency was evaluated by measuring the chemical oxygen demand (COD) of the irradiated dye solutions before and after irradiation. The COD measurements were performed by using an open reflux, dichromate titrimetric method as described in standard methods[28].

RESULTS AND DISCUSSION

Effect of time and temperature on the grafting process

Effect of polymerization time on (grafting yield, grafting efficiency and homopolymer) percentages (G%, GE% and H%) was investigated. Figure 1 illustrates these results at constant monomer and initiator concentrations; [M] = 2×10^{-3} M, [I] = 1.5×10^{-3} M, at 70 °C, respectively after 420 minutes of reaction time. It is shown that both the grafting yield and its efficiency increased with the increment of polymerization time till reaching 7.1% and 2.9 % respectively after 300 minutes. After this time, the percentages of both G and GE tended to increase slowly. Considering the formation of homopolymer; the H% increased as the polymerization time increased. This could be explained on the basis of the increase of number of monomer and initiator molecules that can diffuse onto the surface of PET flakes with proceeding in the reaction time. The tendency to leveling off for the G% and GE% after 300 minutes may be due to the increase

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in the formed homopolymer that can make a diffusion barrier on the PET flakes. The lower increase in G and GE percentage can be also rationalized by the difficulty of monomer molecules diffusion caused by the increase in the medium viscosity.
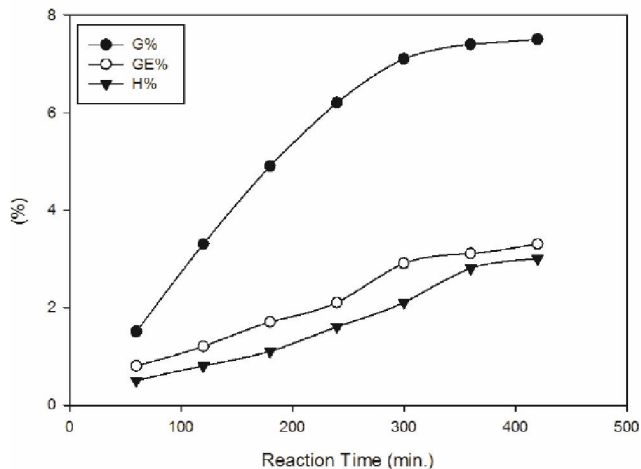

Figure 1 : Variation of G%, GE% and H% with time at [M] = 2 x 10⁻³ M, [I] = 1.5 x 10⁻³ M, at 70 ºC

Considering the effect of temperature on both grafting yield and grafting efficiency percentages in addition to the percentage (%) of the formed homopolymer; Figure 2 represents these results at constant monomer and initiator concentrations 2x 10⁻³ mol/L and 1.5x10⁻³ mol/L respectively after 300 minutes of polymerization time. As shown in Figure 2, the graft copolymerization reaction was assisted at 50 - 80 ºC. It is obvious that, the grafting yield % increased as the reaction temperature increased in the range of 50 - 70 ºC followed by a leveling off. These results were obtained using the aforementioned monomer and initiator concentrations that are considered as the optimum conditions of the reaction. The increase in the grafting yield % with the increase of the applied temperatures may be due to the enhancement in the mobility of both initiator and EMA monomer molecules in the reaction medium. This high mobility may lead to more diffusion rate of the initiator and monomer molecules from the solution phase to surface of PET. Simultaneously, the elevation of the reaction temperature increases the active sites in the reaction medium leading to an increment in the rate of initiation and propagation steps. The lower increase in both the grafting yield and efficiency percentages after 70 ºC can be attributed to the observable increase in the formed homopolymer that may retard the graft copolymerization reaction.
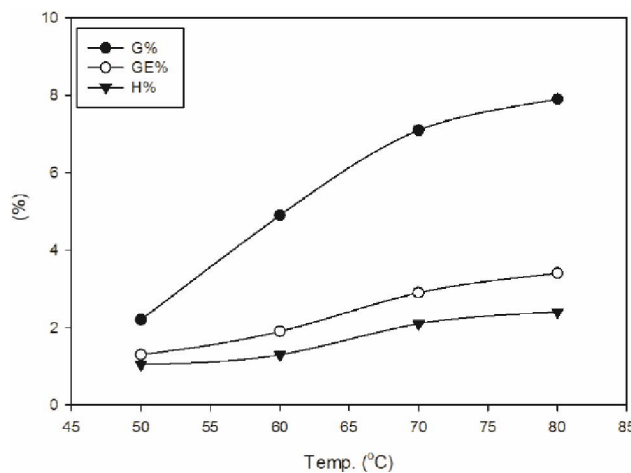

Figure 2 : Variation of G%, GE% and H% with temperature at [M] = 2 x 10⁻³ M, [I] = 1.5 x 10⁻³ M

Effect of monomer and initiator concentrations on the grafting process

The variation in grafting yield and grafting efficiency and homopolymer % through different concentrations of EMA monomer was investigated by carrying out the graft copolymerization reaction using monomer concentration [M] in the range of 0.5 x 10⁻³ - 3 x10⁻³ mol/L. It is obvious in Figure 3 that G% and GE% lifted up with increasing the concentration of monomer. As the EMA monomer concentration boosted, its diffusion on the surface of PET increased leading to an increment in the graft yield. It could be considered that the constancy in both grafting yield and grafting efficiency at higher [M] may be associated with the adsorption of monomer on PET surface in excessive amounts and can prevent more diffusion of the initiator molecules in the reaction medium and thereby retards the grafting process.

TABLE 1 signifies the effect of initiator concentration on grafting yield, the graft efficiency and homopolymer percentages keeping the monomer concentration [M] at 2x10⁻³ mol/L. It is obvious that the concentration of potassium persulphate (KPS) as initiator ranging from 0.5 x10⁻³ mol/L to 3x10⁻³ mol/L affected highly the percentages of grafting yield, efficiency and the formed homopolymer. TABLE 1 shows that the grafting yield increased with increasing the (KPS) until reaching the highest grafting yield at 3x10⁻³ mol/L. The increase in the concentration of the initiator led to slower increase in the grafting yield. This may be attributed to the high concentration of the created free radicals in the reaction mixture. Hence, it was followed by generating

a high rate of homopolymer particles in the reaction medium till reaching 2.5% and 3% at initiator concentration of 2.5 x 10^{-3} and 3.0 x 10^{-3} mol/L respectively. In addition, as the increase in the initiator concentration took place, the termination reactions of the growing polymer chains led to the combination of the free radical species generating low molecular weight species[29].

TABLE 1 : Effect of initiator concentration on G%, GE% and H% at [M] = 2 x 10^{-3} mol/L, 300 min. and temperature 70 °C

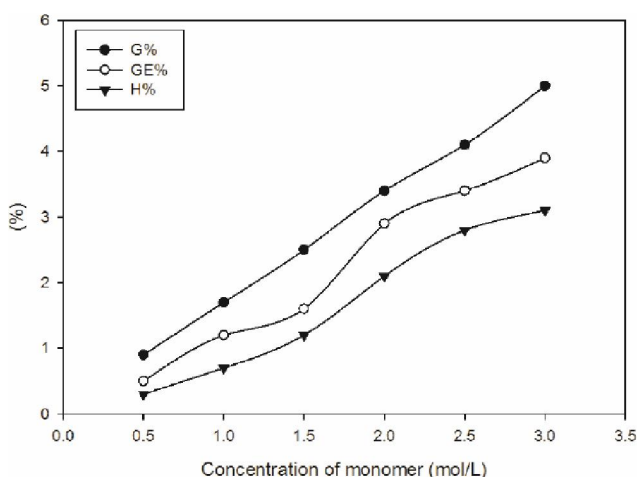| [I] mol/L	G%	GE%	H%
0.5	2.1	1	0.7
1	3.5	1.8	1.5
1.5	7.1	2.9	2.1
2	7.2	3.2	2.3
2.5	7.4	3.4	2.5
3	7.5	3.7	3

Figure 3 : Variation of G%, GE% and H% with concentration of monomer at [I] = 1.5 x 10^{-3} M, at 70 °C after 300 minutes

Effect of TiO$_2$ on the grafting process

At the optimum conditions of the above mentioned grafting copolymerization process of EMA onto PET, the addition of TiO$_2$ and the N-doped one on both G% and GE% have been investigated. Figures. 4 and 5 illustrate the effect of both TiO$_2$ and N-doped TiO$_2$ on G% and GE %. The results clearly reveal that the addition of TiO$_2$ decreased both G% and GE %. This may be attributed to that TiO$_2$ particles increase the viscosity of solution leading to the decrease of the mobility of monomer molecules and the initiator radicals. Moreover, The N-doped TiO$_2$ shows higher G% and GE%

values than those of the anatase one. The N-doped TiO$_2$ has lower band gap energy, so, it may be easily excited by thermal energy effect during the grafting process resulting in formation of excess OH radicals that can be helpful in enhancing the initiation step[30].
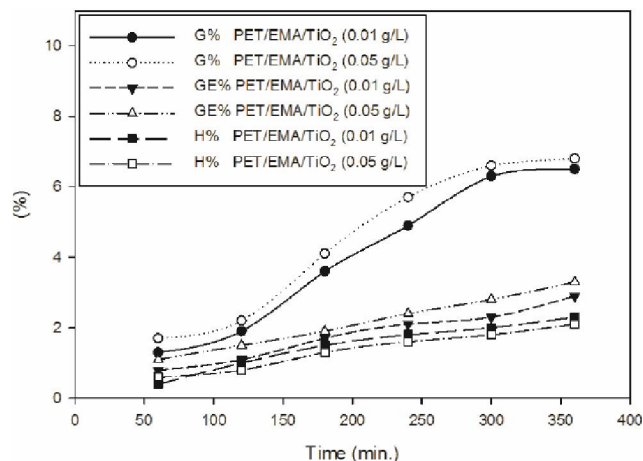

Figure 4 : Variation of G%, GE% and H% with time in presence of 0.01 and 0.05 g/L of TiO$_2$ at [M] = 2 x 10^{-3} M, [I] = 1.5 x 10^{-3} M, at 70 °C after 300 minutes
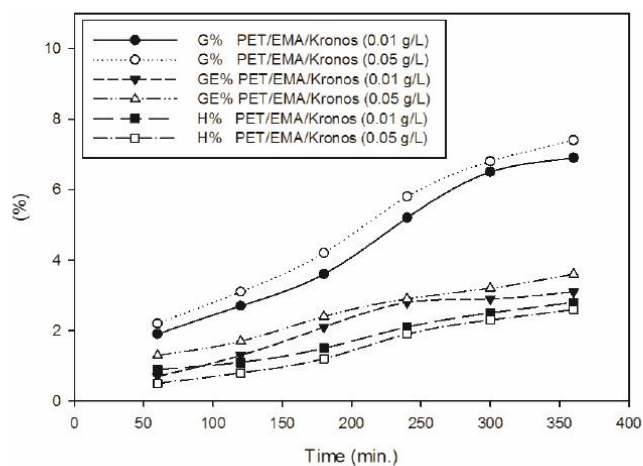

Figure 5 : Variation of G%, GE% and H% with time in presence of 0.01 and 0.05 g/L of Kronos (N-doped TiO$_2$) at [M] = 2 x 10^{-3} M, [I] = 1.5 x 10^{-3} M, at 70 °C after 300 minutes

FTIR and TGA of PET-g-EMA

ATR-FTIR spectra of the PET-g-EMA films are discussed. Figure 6 indicates that the spectrum of the PET-g-EMA film has the distinctive peaks at 1716 cm^{-1} which is common for the stretching vibration of the carbonyl compound of PET and EMA, 1400-1600 cm^{-1}, 2700-2900 cm^{-1} and 3060 cm^{-1} that are typical of C=C, aliphatic C-H and aromatic C-H stretching, respectively. Figure 7 displays illustrative TGA thermograms for PET and its grafted samples. These ther-

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mograms show the variation of the residual weight (RW) % as a measure of the weight loss of the samples and as a function of heating temperature. It is observed that the residual weight % values have a limited amount of weight loss at the initial decomposition temperature, which may be attributed to decomposition of impurities as well as additives. Upon introducing the inorganic TiO_2 either anatase or Kronons, the initial degradation temperature was slightly decreased[31]. The tested samples did not show a significant weight loss until 320°C then decomposition took place. This behavior may be attributed to the fracture of main chains and side groups. The thermal stability of the graft copolymers did not change drastically in presence of TiO_2.
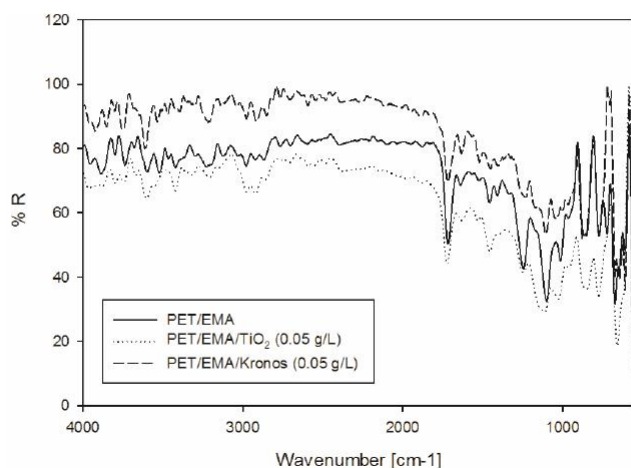

Figure 6 : FTIR spectra of PET/EMA, PET/EMA/TiO$_2$ (0.05 g/L) and PET/EMA/Kronos (0.05 g/L)
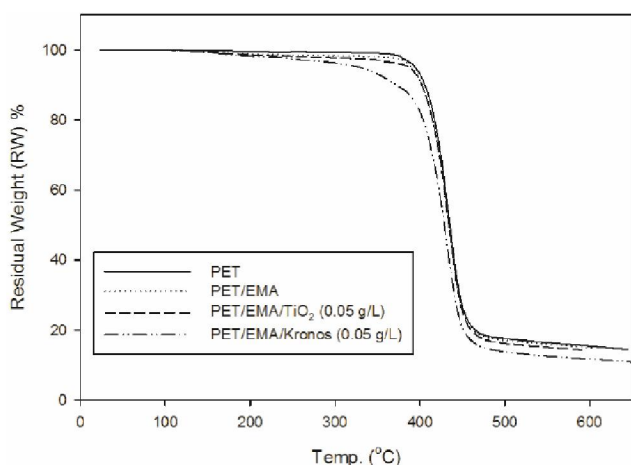

Figure 7 : TGA Thermograms of PET, PET/EMA, PET/EMA/TiO$_2$ (0.05 g/L) and PET/EMA/Kronos (0.05 g/L)

Morphology of PET-g-EMA

The scanning electron micrographs for the freeze-

fractured samples of PET and grafted PET/EMA are illustrated in Figure 8 (a&b) respectively. The ungrafted PET has a smooth and relatively homogeneous appearance. The grafted sample seems to form attached clusters of EMA to the PET matrix in the graft copolymer proving the occurrence of grafting[32]. Some roughness appears in case of presence of 0.01 g/L TiO_2 in the reaction mixture as depicted in Figure 8 (c) as it has more grooves and protrusions on the surface, which increased by increasing the percentage of the added TiO_2 to 0.05 g/L TiO_2 as shown in Figure 8 (d). This roughness signifies the increase in the surface of the grafted copolymer resulted from TiO_2 addition. On the other hand, SEM of PET/EMA in presence of N-doped TiO2 shows more roughness on the grafted surface that increased at the higher concentration of N-doped TiO2 0.05 g/L discernible in the morphology of the grafted surface as shown in Figure 8 (e&f).

Photocatalytic activity of PET-g-EMA

The photocatalytic activities of the samples were evaluated by using the photocatalytic degradation of methylene blue under visible light irradiation. The COD removal efficiency of methylene blue is shown in Figure 9. It could be seen that when methylene blue solution was irradiated in the absence of either TiO_2 or N-doped TiO_2, there was a slight self-degradation after 120 min. In the presence of TiO_2 photocatalyst, an obvious degradation was observed. Moreover, N-doped TiO_2 has better activity for methylene blue degradation than the anatase one. The COD removal exceeded 42%, 46% upon employing 0.01 g/L, 0.05 g/L N-doped TiO_2, respectively. On the other hand, the results of the COD removal showed values of H" 20%, H" 27 % upon using 0.01 g/L, 0.05g/L TiO_2 anatase. It is known that the molecules of methylene blue can be excited by visible light and inject electrons to the conduction band of TiO_2. The injected electrons react with O_2 molecules then adsorbed on TiO_2 surface to yield O_2^- radical anion and subsequently OH radical by protonation[33]. Methylene blue can degrade even in pure TiO_2 system although its photodegradation efficiency is not high. The general rule for semiconductor photocatalysis is that the activity is mainly influenced by three factors: (a) capacity for electron-hole generation, (b) electron transfer route and efficiency (c) separation efficiency of
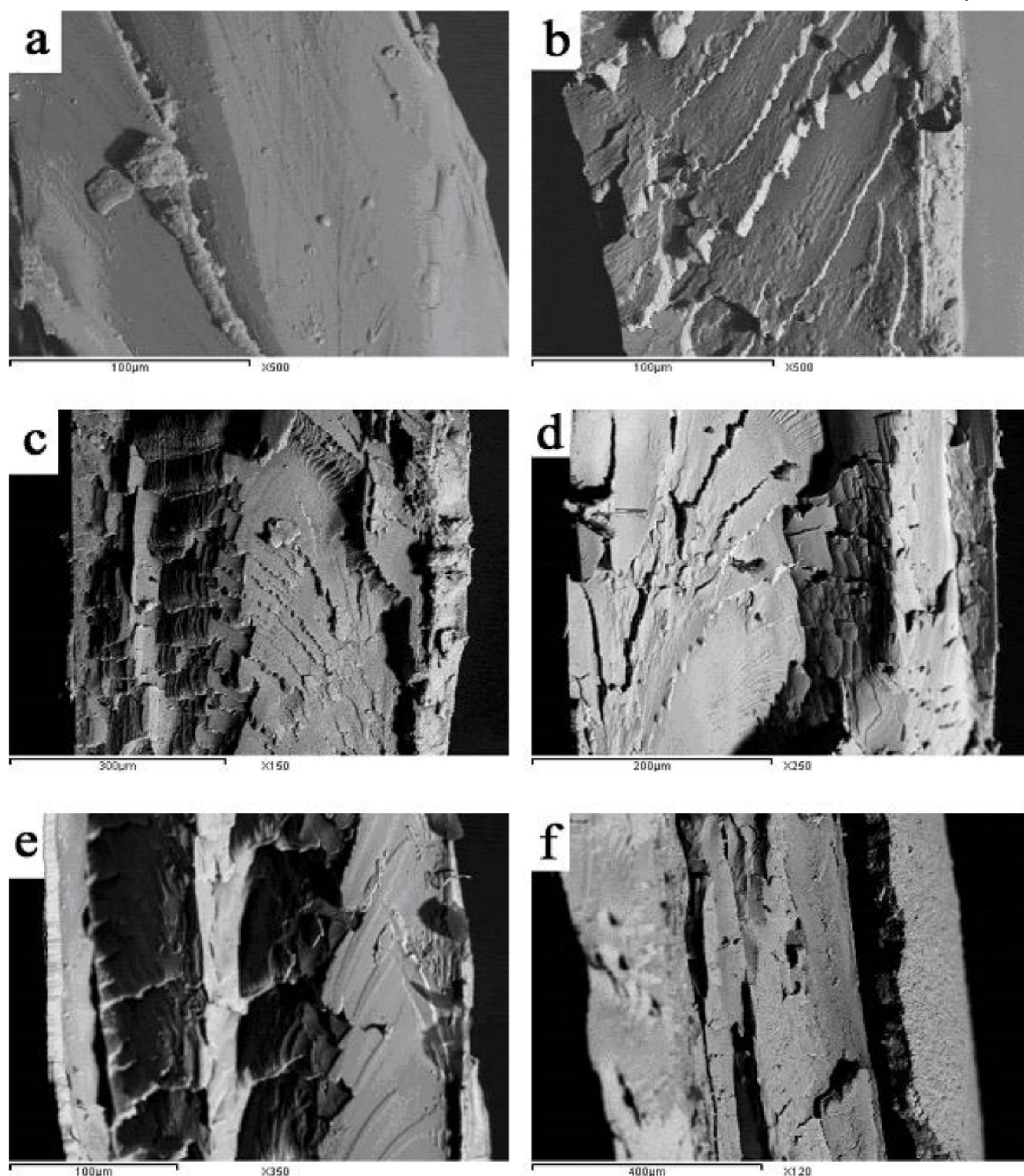
Figure 8 : SEM of a) PET b) PET/EMA c) PET/EMA/TiO₂ (0.01 g/L) d) PET/EMA/TiO₂ (0.05 g/L) e) PET/EMA/Kronos (0.01 g/L) f) PET/EMA/Kronos (0.05 g/L)

photogenerated electron-hole pairs[34,35]. Since pure TiO₂ has a wide band gap, it is difficult to produce electrons and holes under visible light. It is reasonable for pure TiO₂ to have low or no activity for methylene blue

degradation. Upon employing N-doped TiO₂; the recombination of charge carriers effectively decreased after incorporating nitrogen in the TiO₂ lattice. So, more photogenerated charge carriers can participate in or-

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ganic compound degradation, resulting in the enhancement of photocatalytic activity. The presence of nitrogen might improve the migration and separation of photogenerated electrons and holes[36,37].
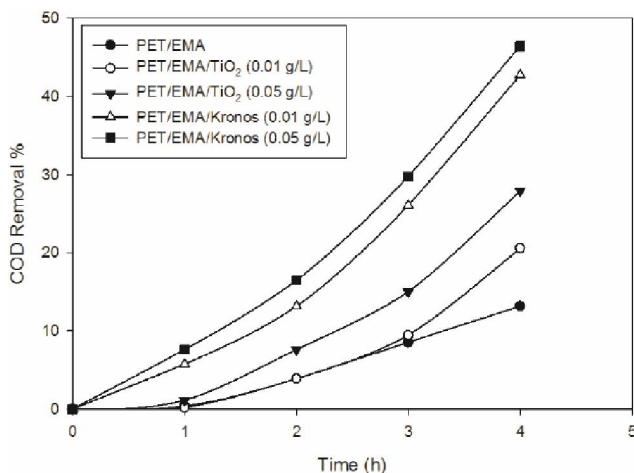

Figure 9 : COD removal % of PET-*g*-EMA, in absence/presence of (0.01 g/L) and (0.05 g/L) of both TiO₂ and Kronos

CONCLUSION

Synthesis of efficient photoactive EMA-*g*-PET was carried out in absence/presence of TiO₂ via copolymerization reaction. Results clearly revealed that both G% and GE% increased with the increase of monomer and initiator concentrations. The optimum G% and GE% were obtained after 300 minutes at 70 ºC. EMA-*g*-PET containing 0.05 g/L of N-doped TiO₂ showed the highest COD removal results among all the investigated samples under solar energy irradiation. This high photocatalytic activity can be recommended to use the aforementioned polymer as a photocatlyst in the removal of the dissolved organic compound from industrial waste water.

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