Functionalized of wax-magnetic nanocomposite \((\text{Fe}_3\text{O}_4/\text{PE})\) pellets by radiation grafting of PAAc for safe dye removal

Mohamed Mohamady Ghobashy

Abstract: Gamma radiation has been used for the fabrication of polyethylene (PE) wax from low density polyethylene pellets composited with 30wt% magnetic oxide \(\text{Fe}_3\text{O}_4\) nanoparticles. The surface of (PE/\text{Fe}_3\text{O}_4) pellets was grafted by acrylic acid AAc using gamma irradiation techniques. A polarity of COOH groups support (PE/\text{Fe}_3\text{O}_4) uses, where functionalization give it facilities to be ready in hydrophilic and/or hydrophobic environments and increasing the capability in adsorbing wide variety of dyes molecules. Wax increases the stability and this will help to improve the recyclability of (PE-g-PAAc)/\text{Fe}_3\text{O}_4;\) recyclability is also helped by \text{Fe}_3\text{O}_4, compared to traditional dye adsorbents. The grafted polyethylene wax can serve as a good adsorbent support for a large variety of dyes. The chemical structure of the modified PE surface was achieved by a grafting process using attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR). Samples of (PE-g-PAAc)/\text{Fe}_3\text{O}_4 have been characterized for water uptake and surface morphology using a scanning electron microscope (SEM); the crystal structure has been determined using X-ray diffraction; and dye removal efficiency was assessed using toluidine blue (TB) as a model.

Keywords: radiation grafting; nanocomposite; pellets; magnetic wax; PAAc

1. Introduction

There are many advantages of radiation grafting over other conventional methods due to its simplicity, and because catalysts and additives are not needed to initiate the grafting reaction (1). Grafting is a process that the polymer acquisition a new feature given them a prioritie to use in a
requisite application. Grafting occurs by monomers covalently bonding onto the polymer chains. This method produces functional groups that adhere to polymer substrates by the strongest chemical bond. Grafted copolymers are promising because they have very different properties to the original polymer before grafting. This article is aimed at the synthesis of magnetic wax (hydrophobic) polymers and coating with a (hydrophilic) layer obtained by grafting of poly acrylic acid (PAAc), using gamma radiation without significant damage to the polymer substrate. Use of this new material will be encouraged for diverse applications in biomedical, catalysis, sensors and dye adsorbent fields. The degree of grafting is adjusted by irradiation dose and monomer concentration with other parameters, e.g. temperature, type of solvent and pH. Gamma irradiation is a promising technique to fabricate a wide range of polymeric materials (2–6) especially to develop selective copolymers for certain applications. The main purpose of the modification is to improve biocompatibility, wettability, mechanical and thermal properties.

Poly ethylene (PE) wax is a synthetic hydrocarbon wax consisting of ethylene monomer chains, and has a comparatively high melting point. PE waxes are compatible with other waxes that are highly hydrophobic. Exposed wax to gamma rays may cause a weight change as a result of radiation-induced oxidation due to oxygen absorption from the surrounding atmospheric. Furthermore, gamma irradiation, especially at high doses above 50 kGy, causes the generation of radiolytic gases such as methane, carbon oxides, and hydrogen, and leads to the formation of cavity and increases the roughness of a surface (7,8). To retain most wax characteristics and also acquire additional properties of the grafted moiety PAAc which hydrophilic in nature. Introducing magnetic oxide (Fe₃O₄) as a composite gives a new material with three phases collected in one.

The PE grafting matrix is a popular subject of research and is used in numerous applications. But grafting of PE wax using acrylic acid that has been grafted onto different polymeric materials has not been done to date. Acrylic acid is pH sensitive and can undergo many chemical reactions to produce new chemical compounds. Due to AAc molecules is good adherent onto almost polymer substrate surface by grafting process induced by gamma radiation.

The main feature of polymer–metal nanocomposite is the stabilization of metal nanoparticles. Different techniques are used to fabricate them, depending on their final application. Fe₃O₄/PE-g-PAAc is an eco-environmental material exhibiting magnetic properties, and is easily recovered using magnets. This feature will be very useful if Fe₃O₄/PE-g-PAAc is used to remove dye from the environment.

In this article, gamma radiation is used for fabrication and modification of PE/Fe₃O₄ magnetic composite wax to enhance dye removal. The surface of PE/Fe₃O₄ was grafted with PAAc so the hydrophilic part comes into contact with the hydrophobic matrixes; thus the new material Fe₃O₄/PE-g-PAAc was used as a dye adsorbent. The modification of the wax surface is of considerable importance for enhanced dye adsorption. The Fe₃O₄/PE-g-PAAc material will be characterized.

2. Material and methods

2.1. Material

LDPE (MFI 7 g/10 min, density 0.925 g cm⁻³, melting temperature (120 °C), was supplied by Exxon Mobil Co., Al-Jubail Saudi Arabia. Black iron oxide/magnetite (Fe₃O₄) powder was from READE Co., Manhattan, USA. Acrylic acid monomer 99% was supplied by Sigma-Aldrich Co, St. Louis, USA

2.2. Preparation of magnetic polyethylene wax (PE/Fe₃O₄) nanocomposite and PAAc grafting process

Preparation procedures of PE wax from LDPE through radiation-thermolysis processes were reported in a previous work (9). Homogenized black pellets of the iron oxide 30% (Fe₃O₄) nanoparticle composite with PE wax were grafted with PAAc using gamma radiation techniques using the following procedures. Radiation-induced grafting is a method to functionalize the surfaces of existing PE/Fe₃O₄ pellets. A weighed amount of PE/Fe₃O₄ pellets and 20% acrylic acid monomer were placed in a test
One ml of 0.1 M FeCl₃ was added to the mixture to prevent homo polymer formation of PAAc, and the mixture was kept at room temperature for 2 h. After that the test tube was exposed to Co-60 gamma cell at dose of 20 kGy with dose rate 2.08 kGy h⁻¹. The product (PE-g-PAAc)/Fe₃O₄ was washed with 0.1 ethanol/water several times, and then dried and again washed with water. The sample was then finally dried in an oven for 3 h at 50°C and further analysis was carried out. The grafting percentage was calculated using the following equation:

\[
\% \text{Graft yield} = \left( \frac{W_g - W_i}{W_i} \right) \times 100
\]

where \( W_i \) is the initial weight of the PE/Fe₃O₄ sample used and \( W_g \) is the weight of the grafted (PE-g-PAAc)/Fe₃O₄ sample after washing and drying.

**Determination of swelling (%)**

\[
\text{Determination of swelling (\%)} = \left( \frac{W_t - W_d}{W_d} \right) \times 100
\]

\( W_t \) is the weight of swelled (PE-g-PAAc)/Fe₃O₄ sample and \( W_d \) is the weight of the initial dry sample.

**2.3. Gamma irradiation**

A cobalt-60 Canadian gamma cell 220 was constructed in the National Centre For Radiation Research and Technology, Nasr City, Cairo with a dose rate of 2.08 kGy s⁻¹ was used.

**2.4. Characterization of magnetize (PE-g-PAAc)/Fe₃O₄ wax nanocomposite property**

**2.4.1. FTIR spectroscopy**

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was conducted on a Vertex 70 FTIR spectrometer equipped with HYPERION™ series microscope (Bruker Optik GmbH, Ettlingen, Germany), over the 4000–400 cm⁻¹ range, at a resolution of 4 cm⁻¹. Software OPUS 6.0 (Bruker) was used for data processing, which was baseline corrected by the rubber band method with CO₂ bands excluded.

**2.4.2. X-ray diffraction**

X-ray diffraction (XRD) patterns were obtained with the XRD-6000 series from Shimadzu Scientific Instruments (SSI), Kyoto, Japan.

**2.4.3. Transmission and scanning electron microscope**

The surface morphology of PE/Fe₃O₄ was evaluated, as well as the degree of dispersion of the Fe₃O₄ nanoparticles in the prepared composites. The dispersion of Fe₃O₄ nanoparticles on the PE matrix was confirmed by the transition electron microscope (TEM) (JEM-100CXII) obtained from JEOL Ltd (Tokyo, Japan). The samples were prepared by placing a melted drop of PE/Fe₃O₄ on a carbon coated copper grid and exposing the grid (200 mesh) to hot air to form a very thin layer of PE/Fe₃O₄ on the grid and examined with resolution: 0.3 nm, magnification:×330–250,000. The effect of gamma radiation on the surface morphology of PE/Fe₃O₄ pellets was examined by SEM model (JSM-5400) from JEOL Ltd.

**3. Results and discussion**

**3.1. Surface morphology of magnetized (PE-g-PAAc)/Fe₃O₄ wax nano composite**

The TEM revealed the size distribution of the Fe₃O₄ nanoparticles composite embedded PE wax varied from 10 to 12 nm, as shown in Figure 1(a). Scanning electron microscopy (SEM) was performed to investigate the surface morphology of unirradiated and irradiated PE/30%Fe₃O₄ wax as shown in Figure 1(b) for the unirradiated samples and Figure 1(c) for the irradiated samples, which become rougher. Figure 1(d) shown the surface of grafting sample (PE-g-PAAc)/Fe₃O₄.
3.2. Crystallinity of magnetic (PE/Fe₃O₄) wax nano composite

From Figure 2 it can be seen that the sites and the intensity of the diffraction peaks are consistent with the standard pattern for (JCPDS-019–0629) with high intensity Bragg peaks at 2θ = 29.82°, 35.7°, 42.2°, 52.6°, and 64.1°, corresponding to the (220), (311), (400), (422) and (440) crystal planes which were the characteristic peaks of standard Fe₃O₄ crystal. The pattern indicates that polyethylene wax with magnetic oxide exhibited or conserved the crystalline structures of both of them. The Bragg peaks in the X-ray diffractogram (Figure 2) for 0 (2θ = 21.1°) and (2θ = 23.29°) is indicative of orthorhombic crystallinity in these samples which correspond to the (110) and (200) planes of PE, and cubic-phase Fe₃O₄.

According to the Debye–Scherrer formula, the crystallite size D_{hkl} for the sample is given by (10):

$$D = \frac{k \times \lambda}{\beta \cos \delta}$$  \hspace{1cm} (3)
A crystallite size (D) of Fe₃O₄ particle can be estimated. Where β is the full width at half-maximum (FWHM) value of XRD lines, Cu Kα radiation is 1.54 Å and K is the shape factor, which can be assigned a value of 0.90, cos θ is the cosine of the Bragg angle and β is the half-height of angle diffraction in radians. Convert β from degree to radians by:

\[ \text{Radians} = \frac{180}{\pi} \text{degree} \] (4)

The crystal size is determined by taking the reflecting peak at 35.7°, which is the characteristic peak of (311) Fe₃O₄. The calculated average crystallite sizes of Fe₃O₄ particles are about 9 nm.

3.3. Chemical modification of PE/Fe₃O₄ by PAAc grafting was performed by FTIR
Radiation grafting of PAAc onto PE/Fe₃O₄ wax nanocomposite is undoubtedly a fascinating field for research as well as a practical way to improve PE wax value. The grafting occurs on the surface of PE wax and not in the bulk. The mechanism of grafting is free radical mechanism. FTIR established that chemical changes were induced onto PE wax. Figure 3 shows the two characteristic peaks for PE wax, located at: 2,914 and 2,847 cm⁻¹, attributed to asymmetric and symmetric CH₂, respectively. Two very low intensity peaks located at 3,034 and 1,373 cm⁻¹ are attributed to the symmetrical
stretching and bending vibration of CH₃, which may be for polypropylene (branched chain) \(^{(11)}\). This indicated that PE wax contained some branched CH₃ molecules, i.e. that polyethylene wax has a degree of branching. Two peaks of PE located at 1,463 and 723 cm\(^{-1}\) are attributed to the spectral vibration of (CH₂) scissoring and rocking, respectively. The peak at 723 cm\(^{-1}\) is chosen to be the internal reference of the polyethylene (and remains unchanged during the grafting reactions). Figure 4 shows the FTIR peaks of the carbonyl group (C = O) located at 1,709 cm\(^{-1}\), indicating that surface grafting of PAAc occurred. Figures 3 and 4 did not differentiate expected in the peak of the carbonyl group (C = O). FTIR spectroscopy was performed in order to prove the formation of Fe₃O₄ as composite with polymer matrix. The FTIR spectrum in Figures 3 and 4 exhibits two peaks at 562 and 620 cm\(^{-1}\); these peaks were assigned to the Fe–O stretching mode of the tetrahedral and octahedral sites \(^{(12)}\).

3.4. Swelling as a function of time

Figure 5 shows the swelling behaviour of PE-g-PAAc/Fe₃O₄ as a function of time. It is observed that the grafted sample show maximum swelling (52%) in 570 min in water at room temperature, indicating that PE wax as completely hydrophobic becomes partially hydrophilic through the grafting of PAAc.
Figure 6(a) and 6(b) shows the images of the irradiated pellet samples of PE/Fe$_3$O$_4$ before and after grafting of PAAc, respectively. In Figure 6(c), the pellets were expanded due to swelling process. Swelled PE pellets containing iron oxide were introduced after PAAc grafting. The pellets swelled by 20 and 52%. Images of the pellets of (PE/Fe$_3$O$_4$) wax in Figure 6 have shown that the swelling is due to the formation of a hydrophilic layer on the surface of the wax.

Figure 7(a) and (b) shows the images of the irradiated pellet samples of PE/Fe$_3$O$_4$ before and after grafting of PAAc, respectively. In Figure 6(c), the pellets were expanded due to swelling process. Swelled PE pellets containing iron oxide were introduced after PAAc grafting. The pellets swelled by 20 and 52%. Images of the pellets of (PE/Fe$_3$O$_4$) wax in Figure 6 have shown that the swelling is due to the formation of a hydrophilic layer on the surface of the wax.

Figure 6(a) shows the rough and cavity for irradiated PE wax pellets + 30% Fe$_3$O$_4$ samples. This cavity of PE surface is beneficial and increasing the grafting percentage for PAAc which reach to 52%. The grafting samples of (PE-g-PAAc)/Fe$_3$O$_4$ led to a significant increase in the hydrophilic characterization of PE wax.
3.5. Testing the dye removal efficiency of PE-g-PAAc

To determine the removal efficiency of 0.05 g PE-g-PAAc as dye adsorbents, 3 ml of test dye solution ($5 \times 10^{-5}$ M) TB was taken (scheme 1). At room temperature the change of colour was observed after 20 min and the difference between (a) PE/Fe$_3$O$_4$ and (b) (PE-g-PAAC)/Fe$_3$O$_4$ in Figure 7 clearly indicated. The adsorbent efficiency of PE/Fe$_3$O$_4$ was enhanced after PAAc grafting and the decolourization reached 78% after 1 h.

4. Conclusion

Radiation-induced grafting of AAc is a successful method for preparing (PE-g-PAAC)/Fe$_3$O$_4$. The grafted PAAc layers introduce a hydrophilic property beside the hydrophilic property of PE wax and Fe$_3$O$_4$ feed magnetic property. This indicates that (PE-g-PAAC)/Fe$_3$O$_4$ can be used as a safe dye adsorbent. Functionalization of PE wax surfaces (PE-g-PAAC)/Fe$_3$O$_4$ shown a removal percentage about 78%.
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