

Preparation and Characterization of Surfactant-Modified Powder Activated Carbon (SM-PAC) Reinforced Poly (Ethylene Oxide) (PEO) Composites

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Poly (ethylene oxide), PEO, which was used for a wide variety of applications is a flexible, crystalline, thermoplastic, water-soluble and non-ionic polymer. The most of studies on surfactant-modified activated carbon (SM-PAC) have been generally focused on the removal of contaminants. This study aims the preparation of PEO/(SM-PAC) composites, using solution-intercalation method. Firstly activated carbon was modified with cationic surfactant, Cetyltrimethylammonium Bromide (CTAB). Then PEO/(SM-PAC) composites were prepared using solution-intercalation method, with two different (SM-PAC) contents (1.0 and 2.0 wt.%). The characterization of the composites was made by X-ray diffraction (XRD), Fourier Infrared Spectroscopy (FT-IR), thermal analysis and tensile tests. The XRD patterns revealed that 2θ positions of the broad peaks belonging to the composites significantly shift to left compared with those of virgin PEO. The SEM images of the surfactant-modified powdered activated carbon (SM-PAC)/PEO composites prepared with the two different SM-PAC contents show that there is an intensive interaction between the CTA^+ ions of modified activated carbon surface and the polymer chains. From the tensile tests, it was found that the unmodified powdered activated carbon dispersed into the polymer matrix made the ductile polymer more brittle. However, the tensile and yield strengths of the composite, prepared with modified powdered activated carbon, have decreased, and the strain percent value has significantly increased.

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1. Introduction

The modification of surface characteristics of solid adsorbents such as powder activated carbon (PAC), using surfactants exhibits a practical importance in terms of industrial and environmental applications [1]. Activated carbon is an amorphous, highly porous carbon material with a high specific surface area [2]. The activated carbon with large surface area, high adsorption capacity, and micro porous structure is one of the most effective adsorbents for organic compounds [3–6], and thus plays an important role in modern science and technology. For instance it is used in the purification of liquids and gases [7, 8], in the catalysis [9, 10], for the separation of mixtures [11, 12], and even in the hydrogen storage [13, 14]. At a cationic surfactant/activated carbon/water system, the surfactant ion or molecules can adsorb onto the surface of the activated carbon through hydrophobic interactions, and hence their hydrophilic parts are oriented toward the aqueous phase [15–20]. Poly (ethylene oxide) (PEO) is the most commercially important polyether. PEO is polymer of ethylene oxide commercially available in the wide range of molecular weights [21]. PEO has $-\text{CH}_3$ end group. PEO is semi-crystalline, biocompatible, biodegradable, non-ionic

and water-soluble polymer of considerable industrial significance which finds applications in many different branches of industry [22]. PEO is currently also used in the pharmaceutical industry for applications such as controlled-release, solid-dose matrix systems, transdermal drug delivery systems and mucosal bioadhesives [23]. PEO is also a very suitable material for hot melt extrusion due to its very good processing ability in different processing conditions, where polymer of low molecular weight can act as a plasticizer for high molecular weight polymer [24]. (PEO)/clay nanocomposites offer new promising materials which display a great potential for use in various application fields [25–26]. The hydrophilic nature and very strong polarity of PEO presents an important advantage when preparing intercalates of PEO and hydrophilic silicate clay platelets [27, 28]. So far, the most of the present studies involving surfactant-modified activated carbon (SM-PAC) have been generally focused on the removal of contaminants. The present study, is aimed on the preparation of PEO/(SM-PAC) composites, using solution-intercalation method. Firstly powdered activated carbon was modified with cationic surfactant, Cetyltrimethylammonium Bromide (CTAB). Then PEO/(SM-PAC) composites were prepared using solution-intercalation method, with two different (SM-PAC) contents (1.0 and 2.0 wt.%). The characterization of the composites was made using X-ray diffraction (XRD), Fourier infrared spectroscopy (FT-IR), thermal analysis and tensile tests.

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2. Materials and methods

2.1. Materials

In this study, Cetyltrimethylammonium Bromide (CTAB) (surfactant or modifier agent) and powdered activated carbon (PAC) (reinforcement filler) were used to produce the polyethylene oxide (PEO) composites. The polyethylene oxide (PEO) with molecular weight of 900.000 g/mol was purchased from Aldrich. The Cetyltrimethylammonium Bromide (CTAB) and dichloromethane (Methylene chloride) were purchased from Merck, and were used without further purification.

2.2. Preparation of surfactant modified activated carbon

Powder activated carbon was modified by adsorption of Cetyltrimethylammonium Bromide (CTAB) at a concentration above critical micelle concentration (CMC) (1.0 g/g powdered activated carbon). For this, 5.0 g of PAC were added to the aqueous solution of 1.0 l, including 5.0 g of CTAB. The mixture was placed in a temperature controlled orbital shaker at 160 rpm and 25 °C for 360 min and left to attain the ambient conditions. Sample was filtered and dried in an oven overnight at 110 °C.

2.3. Synthesis of composites

Polyethylene oxide/surfactant modified powder activated carbon (PEO/SM-PAC) composites were produced by the solution interaction method. The SM-PAC was suspended in Methylene chloride for 10 h in a three-necked flask at ambient temperature and then mixed for 15 min. The PEO/Methylene chloride ratio, 1:33 (g/ml), was maintained by adding an additional quantity of solvent as well as PEO. The flask equipped with a condenser, a mechanical stirrer and a thermometer and its content were then placed in an oil bath heated to 80 °C. The flask was kept under stirring condition for 10 h and then the composites were put into Petri dishes and dried in air overnight at ambient temperature. The same procedure was applied to different SM-PAC ratios (1.0 and 2.0 wt.%).

2.4. Characterization of composites

The composites were analyzed using a Rigaku powder X-ray diffractometer with a Cu K α X-ray source ($\lambda = 1.5406 \text{ \AA}$), and performed at 2 to 40°. The scanning rate of the instrument was 2°/min. FT-IR Spectra of composites were taken on a Perkin-Elmer Spectrum-One by KBr pelletization method from 400 to 4000 cm $^{-1}$. Examination of the samples was done with Scanning Electron Microscope (SEM, 400F model Field Emission SEM). Samples were fixed on SEM stubs with a double sided carbon tape and coated with 5–20 nm thick layer of gold/palladium by sputtering. The thermal stability was tested by thermogravimetric analysis (TGA) using Perkin Elmer TGA-7 at a scan rate of 20 °C/min in nitrogen.

3. Results and discussion

3.1. XRD and SEM analyses

X-ray diffraction (XRD) is one of the most important techniques used for the characterization of composites. Figure 1 shows the XRD patterns belonging to PEO, SM-PAC and SM-PAC/PEO (1.0 and 2.0 wt.%) composites. From this figure, it can be seen that 2θ positions of the broad peaks belonging to the composites have been significantly shifted to the left compared with those of pure PEO. These shifts clearly indicate the textural and conformational change associated with the rearrangement of PEO chains in the case of composite. In the cases of the composites, the characteristic peaks related with CTA $^+$ ions at the modified powdered activated carbon (SM-PAC) have also disappeared. This may imply that there are intensive interactions between the adsorbed CTA $^+$ ions and PEO chains.

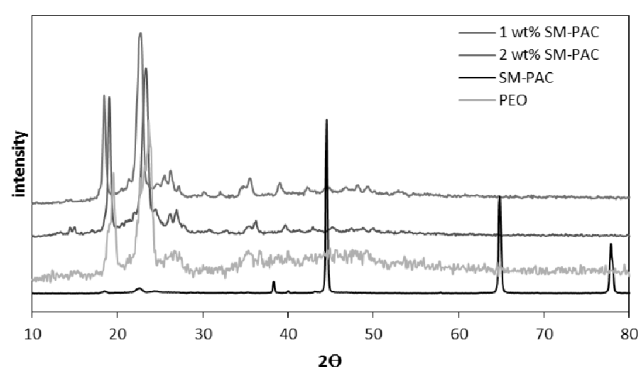


Fig. 1. XRD patterns of pure PEO, SM-PAC and PEO/SM-PAC composites.

SEM images of the samples coded as PAC/CTAB, 1 wt.% PAC/PEO, 1 wt.% SM-PAC/PEO and 2 wt.% SM-PAC/PEO are given in Fig. 2.

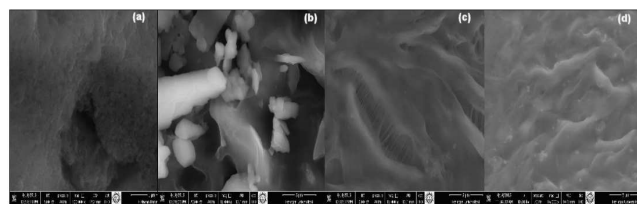


Fig. 2. SEM images of the samples coded as SM-PAC (a), 1.0 wt.% PAC/PEO (b), 1.0 wt.% SM-PAC/PEO (c) and 2.0 wt.% SM-PAC/PEO (d).

The SEM image of the surfactant-modified powdered activated carbon (SM-PAC) demonstrates that there is an effective interaction between CTA $^+$ ions and the activated carbon surface, which has predominantly occurred via the hydrophobic binding. The SEM image of unmodified powdered activated carbon (PAC)/PEO also shows that the adhesive interactions between polyethylene oxide chains and carbon surface are not clearly effective.

The SEM images of the surfactant-modified powdered activated carbon (SM-PAC)/PEO composites prepared in the two different SM-PAC contents, 1 and 2 wt.% (Fig. 2c and 2d), reveal that there is an intensive interaction between the CTA⁺ ions modified activated carbon surface and the polymer chains. Therefore, it can be said that the micelles consisting of CTA⁺ ions have caused a significant change in the arrangement of polymer chains as well as a marked reduction in the polymer/active carbon interfacial energy.

3.2. FTIR analysis

FTIR spectra of pure PEO, PAC/PEO, 1.0 wt.% SM-PAC/PEO and 2.0 wt.% SM-PAC/PEO are given in Fig. 3.

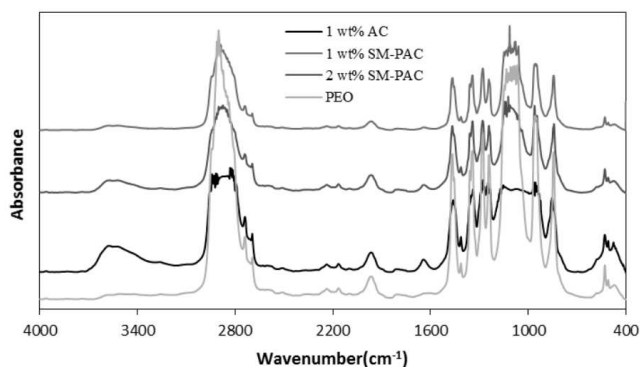


Fig. 3. FTIR spectra of pure PEO, PAC/PEO, 1.0 wt.% SM-PAC/PEO and 2.0 wt.% SM-PAC/PEO.

PEO has a helical structure in the crystalline state. The conformation along this chain is nearly trans (CC-CO), trans (CO-CC) and gauche (OC-CO). The CH₂ rocking modes found in the 1000–700 cm⁻¹ region are particularly sensitive to conformational changes [27]. Pure PEO exhibits a broad band of asymmetric CH₂ stretching between 2945–2891 cm⁻¹ and two narrow bands with lower intensity at 2741–2698 cm⁻¹ [29]. These bands are shifted to 2929–2831 cm⁻¹, 2950–2875 cm⁻¹ and 2947–2893 cm⁻¹ in the cases of 1.0 wt.% PAC/PEO, 1.0 wt.% SM-PAC/PEO, and 2.0 wt.% SM-AC/PEO, respectively. In relation to the CH₂ stretching bands, which appear in the 1468–1242 cm⁻¹ region, the most notable changes occur to the band at 1359 cm⁻¹, which is shifted to 1353–1343 and 1338 cm⁻¹ in 1.0 wt.% PAC/PEO, 1.0 wt.% SM-PAC/PEO, and 2.0 wt.% SM-PAC/PEO, respectively.

3.3. Mechanical analysis

The tensile strength, yield strength and percent strain values of virgin PEO, PAC/PEO, and SM-PAC/PEO composites are given in Table I.

Table I reveals that the values (the tensile strength and the yield strength) obtained from the tensile testing for the PAC/PEO composite (1.0 wt.%) have increased approximately two-fold, but its percent strain value decreased greatly, compared to the pure polymer. This

TABLE I

Results obtained from the tensile tests of pure PEO, PAC/PEO, and two SM-PAC/PEO composites.

Sample	Tensile strength [MPa]	Yield strength [MPa]	% Strain
Pure PEO	0.781	0.547	54.64
1.0 wt.% PAC/PEO	1.45	1.21	24.00
1.0 wt.% SM-AC/PEO	1.38	0.97	82.74
2.0 wt.% SM-AC/PEO	3.82	2.67	95.00

means that the unmodified powdered activated carbon dispersed into the polymer matrix caused it to be more brittle compared to pure polymer. However, the tensile and yield strengths of the composite containing modified powdered activated carbon, at the same ratio with the unmodified powdered activated carbon, have decreased relatively, but percent strain value has significantly increased. Although percent strain is not accepted as an absolute measure for ductility, the increase in its value can be interpreted as though the composite with the capacity to absorb much more deformation energy after the addition of modified powdered activated carbon has gained a higher elastic character. This indicates that the prepared composite with the ratio of 2.0 wt.% of the modified powder activated carbon has been significantly reinforced, showing remarkable improvements in the ductility of polymer.

3.4. Thermal analysis

The results obtained by the DSC analysis of pure PEO, PAC/PEO, and two SM-PAC/PEO composites are given in Table II. This table shows that values of the crystallinity percentage for PAC/PEO composite (1.0 wt.%) and two other composites approximately have increased two-fold but their T_m values have decreased slightly, compared to those of the pure polymer. This indicates that the modified and unmodified powdered activated carbon has caused a conformational change which leads to a more ordered rearrangement of the polymer chains.

TABLE II

Results from DSC analysis of pure PEO, PAC/PEO, and two SM-PAC/PEO composites.

Sample	T_m [°C]	ΔH_m [J g ⁻¹]	Crystallinity [%]
Pure PEO	66.72	101.65	43.87
1.0 wt.% PAC/PEO	69.60	176.00	76.00
1.0 wt.% SM-AC/PEO	67.70	164.00	71.00
2.0 wt.% SM-AC/PEO	68.60	169.00	73.00

4. Conclusions

The main results of this study are summarized below:

- SM-PAC/PEO composites were successfully prepared and characterized.

- The SEM images of the surfactant-modified powdered activated carbon (SM-PAC)/PEO composites prepared in the two different SM-PAC contents show that there is an intensive interaction between the CTA⁺ ions of modified activated carbon surface and the polymer chains.
- The results of the tensile test indicate that very significant improvements in the mechanical properties of composites emerged, compared to those of the pure polymer. This indicates that the presence of activated carbon particles positively affects the conformation of the polymer chains.
- DSC analysis reveals that the modified and unmodified powdered activated carbon causes a conformational change which leads to the more ordered rearrangement of polymer chains.

References

- [1] C. Akmil Başar, A. Karagunduz, B. Keskinler, A. Cakici, *Appl. Surf. Sci.* **218**, 170 (2003).
- [2] H.-J. Hong, H. Kim, Y.-J. Lee, J.-W. Yang, *J. Hazard. Mater.* **170**, 1242 (2009).
- [3] C. Yan, L. Zou, R. Short, *Desalination* **333**, 101 (2014).
- [4] M. Anson, J. Marchese, E. Garis, N. Ochoa, C. Pagliero, *J. Membrane Sci.* **243**, 19 (2004).
- [5] L. Ballinas, C. Torras, V. Fierro, R. Garcia-Valls, *J. Phys. Chem. Solids* **65**, 633 (2004).
- [6] A. Oh, J. Yun, H.-I. Kim, *J. Polym. Res.* **18**, 2441 (2011).
- [7] D.R. Simpson, *Water Res.* **42**, 2839 (2008).
- [8] L.P. Ma, P. Ning, Y.Y. Zhang, X.Q. Wang, *Chem. Eng. J.* **137**, 471 (2008).
- [9] D. Mehandjiev, M. Khristova, E. Bekyarova, *Carbon* **34**, 757 (1996).
- [10] H. Fukuyama, S. Terai, *Catal. Today* **130**, 382 (2008).
- [11] L.S. Chan, W.H. Cheung, S.J. Allen, G. McKay, *Sep. Purif. Technol.* **67**, 166 (2009).
- [12] H. Naono, M. Hakuman, M. Shimoda, K. Nakai, S. Kondo, *J. Colloid Interface Sci.* **182**, 230 (1996).
- [13] J. Hu, Q.M. Gao, Y.H. Wu, S.Q. Song, *Int. J. Hydrogen Energy* **32**, 1943 (2007).
- [14] L. Feng, J. Zheng, H. Yang, Y. Guo, W. Li, X. Li, *Solar Energ. Mat. Sol. C.* **95**, 644 (2011).
- [15] K. Baek, B.-K. Kim, H.-J. Cho, J.-W. Yang, *J. Hazard. Mater.* **99**, 303 (2003).
- [16] H.-D. Choi, M.-C. Shin, D.-H. Kim, C.-S. Jeon, K. Baek, *Desalination* **223**, 290 (2008).
- [17] C.A. Basar, C. Aydiner, S. Kara, B. Keskinler, *Sep. Purif. Technol.* **48**, 270 (2006).
- [18] K. Baek, B.-K. Kim, J.-W. Yang, *Desalination* **156**, 137 (2003).
- [19] K. Baek, J.-W. Yang, *Desalination* **167**, 101 (2004).
- [20] H.-D. Choi, J.-M. Cho, K. Baek, J.-S. Yang, J.-Y. Lee, *J. Hazard. Mater.* **161**, 1565 (2009).
- [21] J. Kahovec, R.B. Fox, K. Hatada, *Pure Appl. Chem.* **74**, 1921 (2002).
- [22] K. Pielichowski, K. Flejtuch, *J. Anal. Appl. Pyrol.* **73**, 131 (2005).
- [23] M.M. Crowley, F. Zhang, J.J. Koleng, J.W. McGinity, *Biomaterials* **23**, 4241 (2002).
- [24] N.S. Vrandecic, M. Erceg, M. Jakic, I. Klaric, *Thermochim. Acta* **498**, 71 (2010).
- [25] M.M.E. Jacob, E. Hackett, E.P. Giannelis, *J. Mater. Chem.* **13**, 1 (2003).
- [26] Z. Shen, G.P. Simon, Y.-B. Cheng, *Polymer* **43**, 4251 (2002).
- [27] W. Loyens, P. Jannasch, F.H.J. Maurer, *Polymer* **46**, 915 (2005).
- [28] P. Meneghetti, S. Qutubuddin, *J. Colloid Interface Sci.* **288**, 387 (2005).
- [29] P. Aranda, E. Ruiz-Hitzky, *Acta Polym.* **45**, 59 (1994).