

Synthesis of New Cationic Surfactants Based on Recycled Poly(ethylene terephthalate) for Deinking of Solvent-Based Ink from Low-Density Polyethylene Surface

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ABSTRACT: Water-soluble oligomers based on poly(ethylene terephthalate) waste, PET, were prepared from transesterification of PET with diethanolamine and triethanolamine in the presence of manganese acetate as a catalyst at temperature of 200°C for 8 h. New cationic surfactants were prepared by reaction of the produced recycled oligomers with bromoacetic acid followed by quaternization with pyridine. The chemical structure of the prepared surfactants was confirmed by ¹H-NMR analysis. The surface tension, critical micelle concentration, and surface activities were determined at different temperatures. Surface parameters such as surface excess concen-

tration (Γ_{\max}), the area per molecule at interface (A_{\min}), and the effectiveness of surface tension reduction ($[\Gamma]_{\text{CMC}}$) were determined from the adsorption isotherms of the prepared surfactants. The prepared surfactants were tested as ink removal for printed low-density polyethylene surface. The effect of surfactants concentrations, pH, soaking time, and shaking time were investigated for deinking process. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1160–1172, 2010

Key words: cationic surfactant; PET waste; glycolysis; recycling; deinking; solvent-based ink; LDPE film

INTRODUCTION

Poly(ethylene terephthalate), PET, has been known for many years simply as a textile fiber forming material. The main growth now observed in the PET market is due to films, bottles, sheets, and coating products, which came into existence in 1970s.¹ PET is widely used in packaging applications, especially in water and soft drink bottles replacing poly(vinyl chloride) and glass bottles because of its clarity, lightweight, and selective gas permeability.² As PET bottles do not readily decompose in the nature, the disposal of a large amount of PET bottles has caused serious environmental and space problems. Because of the reprocess difficulty of PET and the stringent regulation of Food and Drug Administration that does not recommend recycled materials for direct contact with food products,³ PET waste can be chemically recycled through chemical reactions into new useful resins such as epoxy, polyurethane, vinyl ester and unsaturated polyester resins.^{4–8}

The most common polymers used for plastic film production include low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyvinyl chloride, and polypropylene. The increased environmental pressure to minimize solid waste and the reduced need for raw materials gives incentives for recycling rather than landfilling.⁹ It has been reported that the recycled plastics often bear poor physical and mechanical properties when compared with virgin one.^{10,11} One such cause of the deterioration in the properties is the ink that is normally present on plastic surface. For polyethylene film, it has been shown that the physical properties of recycled polymer are similar to that of virgin polymer if ink is first removed from the film.¹² One traditional method of ink removal is to clean the plastic surface with hazardous solvents such as hexane or members of its homologous series. However, the vapor from these solvents used in an enclosed plant may not meet modern indoor air quality standards,¹³ and most solvents used in industry are toxic. Alternative deinking process using surfactants in aqueous solution found desirable progress because of their biodegradability, nontoxicity, and nonvolatility. Previous studies on the effect of surfactant types on deinking of polyethylene films have shown that cationic surfactants are more effective than anionic and nonionic surfactants and have the same effectiveness as amphoteric surfactants.¹⁴ In this respect, this

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study aims to prepare new cationic surfactants from esterification of bromoacetic acid with glycolized oligomers of PET waste either with diethanolamine (DEA) or triethanolamine (TEA). The bromoacetic ester is then replaced by reaction with pyridine. The effects of important parameters are quantified by simple soaking and shaking time parameters. The effects pH of medium, chemical structure of these cationic surfactants, and their concentrations on deinking of LDPE sheets are another goal of this study.

EXPERIMENTAL

Materials

PET beverage bottles were collected from waste. They were crushed to small pieces after washing with soap and methanol and removing of adhesive materials. The intrinsic viscosity of PET in was found to be $0.015 \text{ dm}^3 \text{ kg}^{-1}$ and measured at 25°C in a 40–60 w%/w% phenol–ortho-chlorophenol mixture.¹⁵ The Mark-Houwink parameters k and a 40–60 w%/w% phenol–ortho-chlorophenol mixture were determined as 0.00372 mL/g and 0.73 , respectively.¹⁵ The average number molecular weight, M_n , and weight average molecular weight, M_w , were measured by gel permeation chromatography, GPC, Water model 600 E using 30–70 vol/vol phenol–chloroform mixture at 40°C . M_n and M_w data were $31,600$ and $63,200 \text{ g mol}^{-1}$, respectively. DEA, TEA, bromoacetic acid, pyridine (Pyr), *p*-toluene sulfonic acid (PTSA), and manganese acetate were used as supplied from Aldrich Chemicals Co.

Printed LDPE film was supplied by a local printing press in Egypt. It was printed with blue solvent-based ink using Flexographic printing press after surface treatment with corona discharge.

Techniques

Synthesis of cationic surfactants from PET waste

PET waste was depolymerized with DEA and TEA using 1 : 1.23 and 1 : 1.63 mole ratios, respectively. The reaction was carried out in the presence of 0.5% (by weight) of manganese acetate based on the weight of PET in a nitrogen atmosphere at 180°C for 4 h, and then at 190 – 200°C for 3 h. The produced oligomers were purified as described in previous publications.^{6,16,17} The purified oligomer of glycolized PET waste with DEA and TEA were abbreviated here as GD and GT, respectively. The purified oligomers were analyzed to determine the hydroxyl value by the conventional acetic anhydride/pyridine method.¹⁸

Esterification of 1 mol of GD and GT with bromoacetic acid was completed using 2 and 4 mol of bro-

moacetic acid, respectively. PTSA (1% weight percentage based on weight of GD or GT and bromoacetic reactants) was used as catalyst. The reaction mixture was stirred, and the temperature of reaction was increased up to reflux temperature for 4 h with azeotropic removal of water. The products were poured in threefolds of cold water to remove unreacted GD, GT, and PTSA. The precipitates were filtered and washed with water until the neutral filtrate obtained. The solid products were dried in vacuum oven at 60°C . The purified esters of GD and GT were abbreviated as GD-Br and GT-Br, respectively.

Quaternization 0.1 mol of GD-Br and GT-Br was completed using 3 and 5 mol of pyridine, respectively. Toluene was used as solvent, and the concentration of reactants in reaction mixture was 35% (w/v). The reaction mixture was refluxed for 2 h. The crude products were purified by washing with petroleum ether and dried in vacuum oven at 35°C . The prepared surfactants were dissolved in CDCl_3 and analyzed using Jeol NMR spectrometer model JNM-EX (270 MHz) (Jeol, USA) as another spectroscopic technique for determining the chemical structures. The purified compounds were analyzed using ATI Mattson Genesis Series FTIR spectrophotometer (Thermo Electron Corp., USA). The prepared cationic surfactants of pyridine quaternized GD-Br and GT-Br were designated as GD-Pyr-Br and GT-Pyr-Br, respectively. The prepared cationic surfactants were dissolved in water/2-propanol mixture, (volume ratio 70/30) at concentration of weight percentage of 50%.

Ink analysis

The ink was evenly pasted onto a $15 \text{ cm} \times 20 \text{ cm}$ glass plate. The layer of ink was made as thin as possible to speed up the drying. The painted glass was later dried in an oven at 60°C over night, after that the ink was scraped off from the glass surface and ground in a mortar. The chemical composition of the ink was investigated by a Fourier-transformed infrared spectrometer.

Deinking experiments

Surfactant solutions were always prepared fresh for each experiment in acidic medium using hydrochloric acid for GT-Pyr-Br and sodium hydroxide for GD-Pyr-Br as both surfactants were not soluble in pure water. Both types of surfactants were prepared at various concentrations (0.125, 0.25, 0.5, 1, 2, and 4 CMC) to investigate the effects of surfactant concentration, soaking and shaking time, pH on deinking efficiency. Several trials have done to determine the optimum shaking and soaking time for different

aqueous pH solutions. The printed part of the film was cut into 25 mm × 25 mm pieces. Each five printed pieces were soaked (without shaking) for 1 h in 40 mL surfactant solution in a plastic container for each parameter. After soaking, the plastic containers having small irregular shapes of coarse silica aggregates were shaken in a laboratory ball mill for 1 h to study the effect of pH. These silica aggregates were used as the abrasive material to facilitate the detachment of ink from the plastic surfaces. To study the effect of soaking time, the printed samples were soaked at various times (from 0 to 6 h) and were shaken for 1 h. The plastic containers were allowed to shake for various shaking times (from 1/2, to 3 h) after soaking for 1 h to investigate the shaking time parameters. After shaking, the samples were removed from the plastic containers, washed several times with distilled water, and air-dried. Each experiment was repeated at least twice. Blank experiments were conducted via soaking the printed samples in HCl and NaOH for 1 h and then shaking for 1 h.

Characterization

The average number molecular weight of the glycolyzed PET products was measured by GPC Water model 600 E using 30–70 vol/vol phenol–chloroform mixture at 40°C. Surface tension measurements were performed using a DU Nouy Tensiometer (Kruss Type 8451) for various concentrations of surfactants. Doubly distilled water and 2-propanol mixture (volume ratio of water : 2-propanol 70 : 30) was used to dissolve the prepared surfactants.

The amount of ink on the plastic film before and after deinking was detected by measuring the print density using RCP portable colors reflection densitometer, with an accuracy of ± 0.02 density units. Before using the densitometer, it was zero adjusted and calibrated. The percentage ink removed was determined from the print density readings.

The deinked plastic (PE) samples were evaluated using Elrepho 450X dual beam spectrophotometer (diffused illumination and 0° viewing area). The spectral analyzer with its high resolution holographic grating performs a spectral scan of 360–700 nm using 10 nm measurement intervals. The illuminant source was D65, representing daylight with a correlated color temperature of 6500 K. The CIELAB (L*, a*, b*) color scale was chosen to specify the sample colors. The total color difference between standard (clear film) and sample (printed or deinked film) can be quantified by a single parameter (DE*) to indicate the degree of deinking.

The DE* is calculated as¹⁹:

$$DE^* = [(DL^*)^2 + (Da^*)^2 + (Db^*)^2]^{1/2}$$

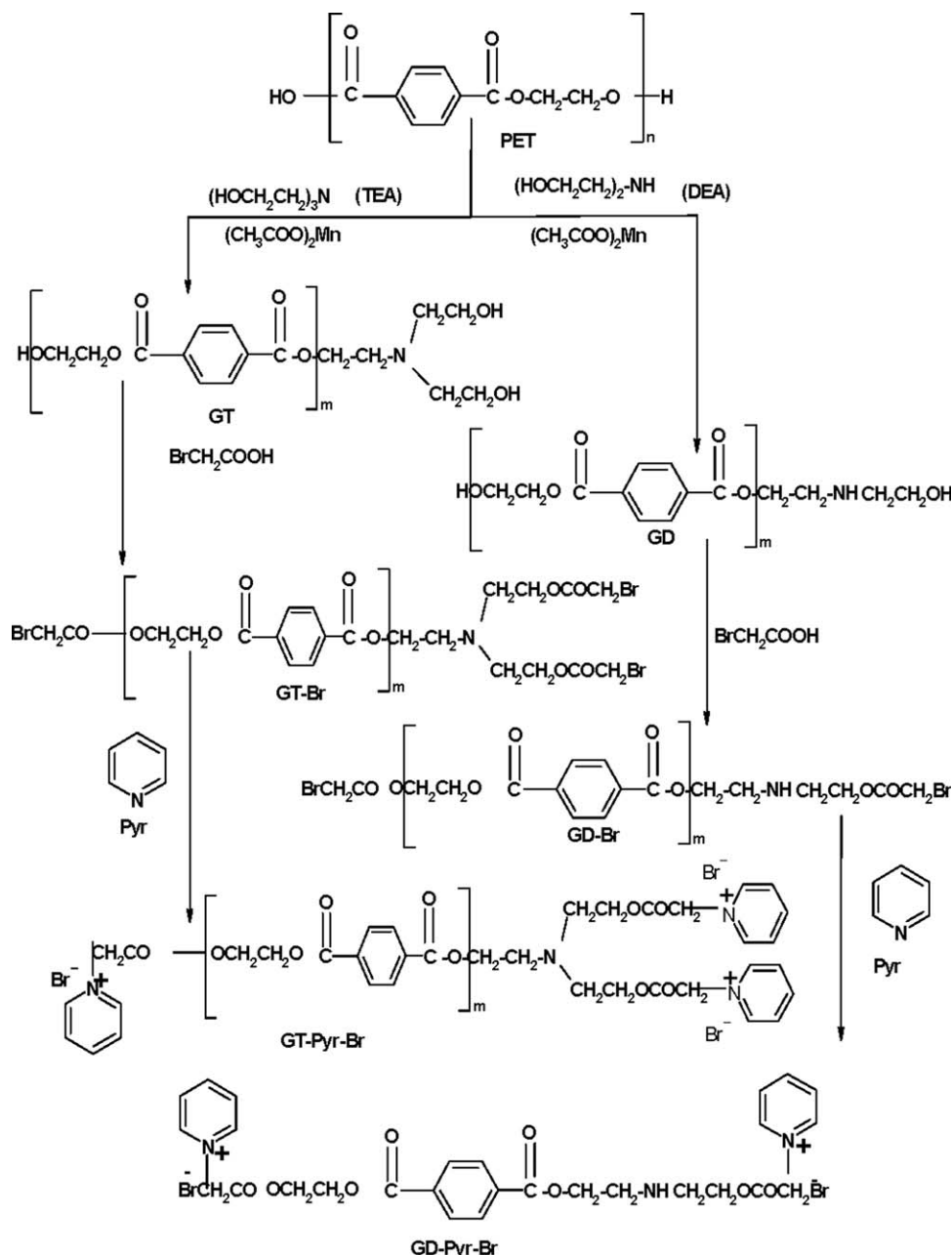
where

$$(DL^* = L^*_{\text{sample}} - L^*_{\text{standard}}), (Da^* = a^*_{\text{sample}} - a^*_{\text{standard}}), (Db^* = b^*_{\text{sample}} - b^*_{\text{standard}}).$$

RESULTS AND DISCUSSION

The glycolyzed products, designated GD and GT, were obtained by depolymerization of PET with DEA and TEA, respectively. Glycolysis consists of the *trans*-esterification of PET and the depolymerization of its polymer chain to low-molecular-weight oligomers. The scheme of glycolysis is represented in Scheme 1. The oligoesters have two hydroxyl end groups, i.e., oligoester diols are formed. The temperature of the glycolysis of PET with DEA and TEA must be fixed at 200°C throughout the reaction to prevent the formation of alicyclic derivatives between hydroxyl groups of the produced polyhydroxy glycolyzed PET.^{20,21} The glycolyzed product was analyzed for hydroxyl values (in mg KOH g⁻¹) after removal of free DEA. The molecular weights of the glycolyzed PET with DEA and TEA were determined by GPC as described in previous works.^{17,20,21} The structure of the PET oligomers with DEA and TEA was determined by FTIR and ¹H-NMR spectroscopy.^{17,20,21} The data revealed that the amounts of glycol consumed in producing GD and GT were 10.77 and 13.02%, respectively. The molecular weights of the GD and GT were determined by GPC as described in the experimental section. The average molecular weights of GD and GT were 957 and 1131 g mol⁻¹, respectively.¹⁷ The structures of the GD and GT were verified from their FTIR spectra. The spectra of GD and GT were not represented for brevity. The presence of strong band at 3450 cm⁻¹, in all spectra, indicated the termination of the glycolyzed products with hydroxyl groups. On the other hand, the band observed at 810 cm⁻¹ for all depolymerized PET is assigned to —CH out-of-plane bending of *p*-substituted phenyl. This band confirmed the presence of phenyl rings in depolymerized products. The presence of strong peaks at 1745 and 1150 cm⁻¹, which were assigned for C=O stretching and C—O stretching of ester groups, indicated the incorporation of ester groups in all depolymerized PET products.

A further confirmation for glycolysis of PET with DEA and TEA was determined by ¹H-NMR. The signals at chemical shifts 8, 4.8, and 4.3 ppm, represented *p*-substituted phenyl group, —OOCCH₂CH₂COO— and —OCH₂CH₂N— of glycolyzed PET, respectively, were observed in all spectra. The appearance of signal at 2.6 ppm in the spectra of GD and GT, which represent OH group of glycolyzed



Scheme 1 Synthesis of cationic surfactants based on GD and GT oligomers.

DEA and TEA, indicated that the produced oligomers have a terminal hydroxyl groups as represented in Scheme 1. Accordingly, the terminal hydroxyl alcohol of both GD and GT can be used to esterify with bromoacetic acid to produce cationic surfactants which is discussed in the forthcoming section.

Synthesis of cationic surfactants

This work deals with the synthesis of cationic surfactants by esterification of dihydroxyl- or tetrahydroxyl-oligomer of GD and GT with bromoacetic acid to produce GD-Br and GT-Br ester. The bromine atom of ester was then replaced by reaction with pyridine to produce

GD-Pyr-Br and GT-Pyr-Br cationic surfactants. The chemical structure of the prepared surfactants was represented in Scheme 1. The structures of the produced surfactants were confirmed using FTIR spectroscopy. The FTIR spectrum of GT-Br was selected and represented in Figure 1(a), and it was observed that the spectra of GD-Br and GT-Br are nearly identical. The presence of stretching bands at 1745 cm⁻¹ for the ester carbonyl (C=O) and absence of the peak at 3450 cm⁻¹ (OH stretching) indicated the esterification of both GD and GT with bromoacetic acid. The band at 810 cm⁻¹ in the spectra of GD-Br and GT-Br was assigned to C–H out-of-plane bending for *p*-substituted aromatics. The appearance of this band confirmed the incorporation of

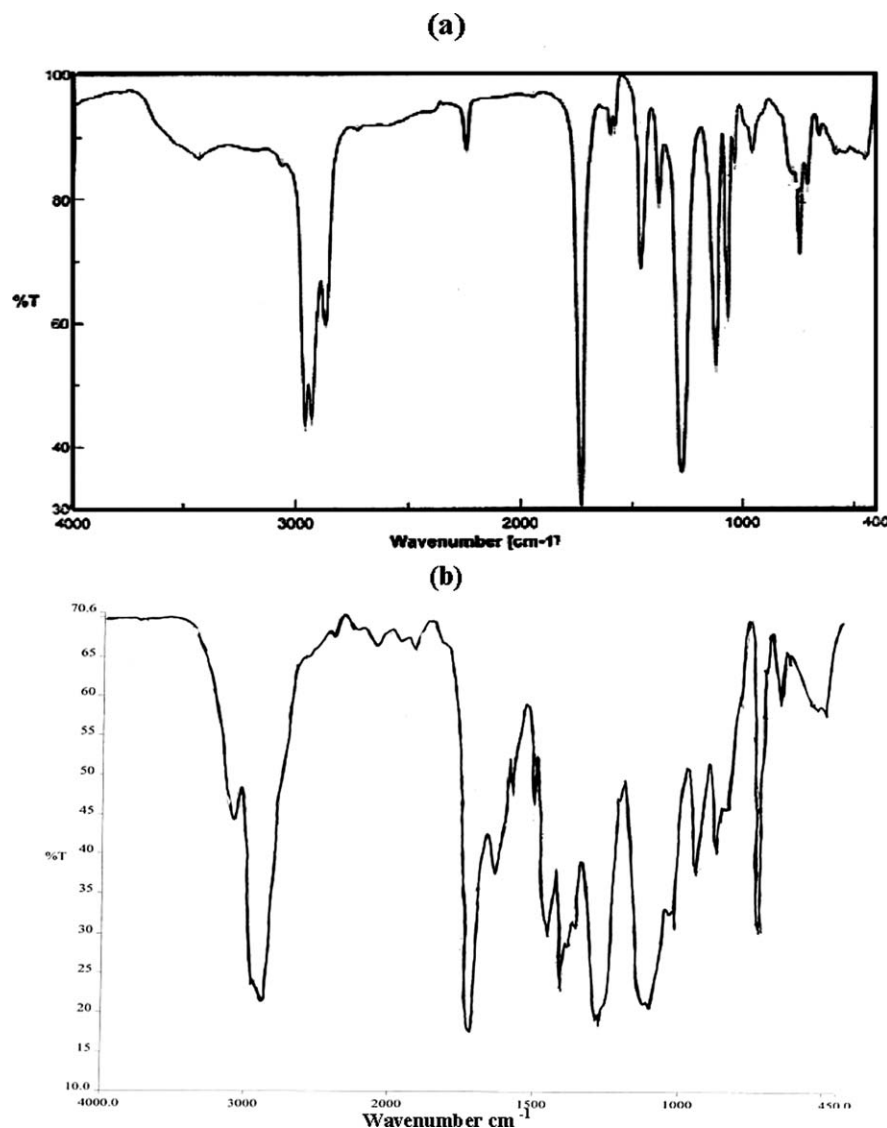


Figure 1 FTIR spectra of (a) GT-Br and (b) GT-Pyr-Br oligomer.

the PET backbone in all cases. The appearance of band at 550 cm^{-1} in spectra of both GD-Br and GT-Br can be attributed to C—Br stretching band, and this band confirmed the incorporation of Br in both GD-Br and GT-Br derivatives. The chemical structure of the prepared cationic surfactant, based on quaternization of pyridine with GD-Br and GT-Br oligomers, was confirmed by IR analysis. In this respect, IR spectrum of GT-Pyr-Br was selected and represented in Figure 1(b). The appearance of new four bands at 1400 , 1460 , 1550 , and 1600 cm^{-1} , which referred to skeletal bands of pyridine, indicated the incorporation of Pyr with both GD-Br and GT-Br oligomers. On the other hand, the appearance of two bands at 710 and 740 cm^{-1} , which attributed to C—H out of plan bending of pyridine, confirmed the quaternization of Pyr with GD-Br and GT-Br oligomers.²²

A further confirmation for formation of quaternized Pyr with GD-Br and GT-Br oligomers was determined from $^1\text{H-NMR}$ analysis. In this respect,

the spectra of GT-Br and GT-Pyr-Br were represented in Figure 2(a,b), respectively. The signals at chemical shifts 8 ppm, 4.8 ppm, and 4.3 ppm, represent *p*-substituted phenyl group, $\text{OOCCH}_2\text{CH}_2\text{COO}$ and $\text{OCH}_2\text{CH}_2\text{N}$ of GT, respectively, were observed in all spectra. The appearance of new signals at 7.2, 7.4, and 8.5 ppm which represent CH=CH Pyr protons, in spectrum of GT-Pyr-Br [Fig. 2(b)] indicates the formation of quaternized cationic derivative.²²

Solubility and surface activity of the prepared surfactants

The proposed mechanism for the removal of a solvent-based ink from polyethylene surface was previously reported.²³ The mechanism consists of four main steps: (1) surfactant adsorption on both printed and unprinted PE surface; (2) solubilization of ink binder in micelles; (3) detachment of ink pigment

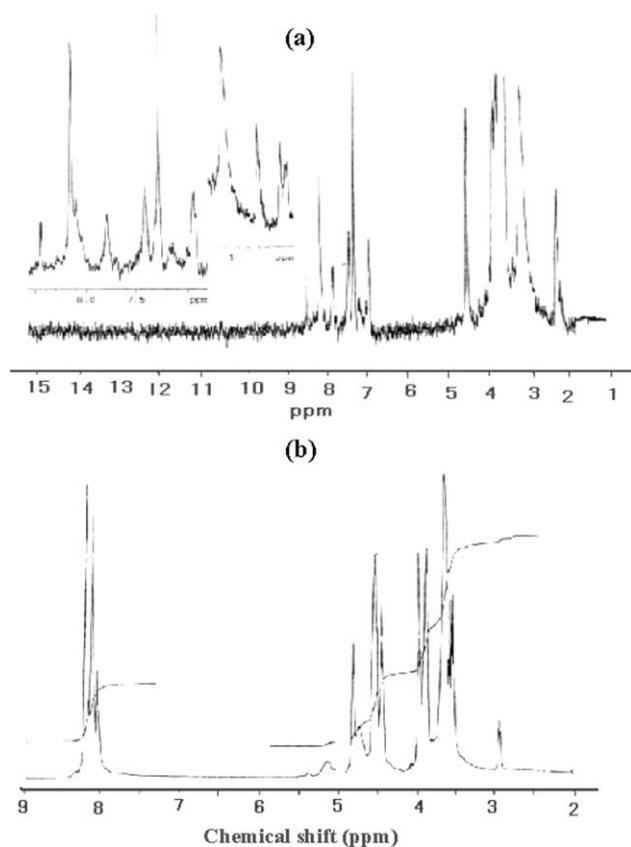


Figure 2 $^1\text{H-NMR}$ spectra of (a) GT and (b) GT-Pyr-Br oligomers.

from PE surfaces; and (4) stabilization and dispersion of the detached ink particles. Several publications reported that the concentration of surfactants, wettability of the surfactant on PE surface, and solubilization of ink binder in the surfactant micelles are important factors for deinking process.^{13,15,23} The deinking began at concentration close to surfactant critical micelle concentration (CMC) and increased significantly at concentrations greater than CMC. It was also reported that the deinking increased with increasing the length of hydrophobic part or hydrophobicity of surfactants. Accordingly, the solubility and surface activity of the prepared surfactant can be evaluated to determine the solubility and aggregations of the surfactants in aqueous solutions. It is well known that modification of a polymer backbone yields different hydrophobicity, chain flexibility, and solubility due to the difference of inter- and intramolecular interactions. In this respect, the prepared surfactants based on PET oligomers are not soluble in cold or hot water. The solubility of the prepared surfactants was increased by mixing water with isopropanol. The suitable mixing ratio of water/2-propanol mixture was 70/30. The solubility and state of polymer solutions should depend on the backbone composition and hydrogen bonds between polar groups of recycled PET oligomers. Consequently,

because of different types of interactions, the solution behavior of PET oligomers is difficult to predict. It is well known that, there are two proposed mechanisms studied the behaviors of the surfactants in the aqueous solutions which based on micellization and adsorption mechanisms of the surfactants. The distortion of the water structure can also be decreased (and the free energy of the solution reduced) by aggregation of the surface-active molecules into clusters (micelles) while their hydrophilic groups are directed toward the water solvent. Micellization is, therefore, an alternative mechanism for adsorption at the interfaces for removing the lyophobic groups from contact with the solvent, thereby reducing the free energy of the system. The micellization and adsorption of surfactants are based on the CMC, which were determined by the surface balance method. The CMC values of the GD-Pyr-Br and GT-Pyr-Br surfactants were determined at 30°C from the change in the slope of the plotted data of surface tension (ST) versus natural logarithm of the solute concentration ($\ln C$). The adsorption isotherm plots of the relation between surface tension (ST) and $\ln C$ were illustrated in Figure 3. This plot is used for estimating the surface activity and confirming the purity of the studied surfactants. It is of interest to mention that all isotherms showed one phase, which is considered as an indication of the purity of the prepared surfactants. The values of CMC for GD-Pyr-Br and GT-Pyr-Br cationic surfactants were listed in Table I. In the previous work, nonionic surfactants based on GD and GT were prepared.^{20,21} By comparing the data of CMC listed in Table I for cationic surfactant GD-Pyr-Br and GT-Pyr-Br and nonionic, which previously prepared, it was found that the cationic surfactants have higher CMC values. These data can be referred to the solubility differences between both cationic and nonionic surfactants. GD-Pyr-Br surfactant possesses high CMC value than GT-Pyr-Br which reflected to increase the solubility of GD-Pyr-Br in water/2-propanol. This can be attributed to the formation of more active cationic sites in GT-Pyr-Br than GD-Pyr-Br surfactants. It was previously reported that the number of ionic group in the surfactants molecule affects the CMC value.²⁴ In this work, the steric hindrance between cationic sites of GT-Pyr-Br is expected to be larger in comparison with GD-Pyr-Br as described in Scheme 1. This may also decrease the CMC values with increasing number of such groups substituted on the cationic sites.²⁵

When comparing the performance of different surfactants at interfacial phenomena, as in most phenomena, it is necessary to distinguish between the amount of surfactant required to produce a given amount of change in the phenomenon under investigation and the maximum change that the surfactant

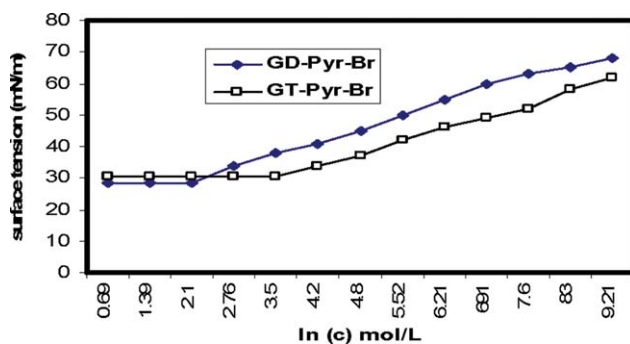


Figure 3 Adsorption isotherms of GD-Pyr-Br and GT-Pyr-Br surfactants. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

can produce, regardless of the amount used. The former parameter is the efficiency of the surfactant and the latter is its effectiveness. These two parameters do not necessarily run in parallel to each other in surfactants, and in fact in many cases run counter to each other. The direct determination of the amount of surfactant adsorbed per unit area of liquid–gas or liquid–liquid interface, although possible, is not generally undertaken because of the difficulty of isolating the interfacial region from the bulk phase for purposes of analysis when the interfacial region is small, and of measuring the interfacial area when it is large. Instead, the amount of material adsorbed per unit area of interface is calculated indirectly from the surface or interfacial tension measurements. The concentration of surfactants at the water–air interface can be calculated as surface excess concentration (Γ_{\max}). The surface excess concentration of surfactant at the interface may, therefore, be calculated from surface or interfacial tension data using the equation: $\Gamma_{\max} = -(1/RT)(\partial\gamma/\partial \ln c)$; where $-\partial\gamma/\partial \ln c$ is the slope of the plot of ST (γ) versus $\ln c$ at constant temperature (T) and R is the gas constant (in $\text{J mol}^{-1} \text{K}^{-1}$).²⁶ The surface excess concentration at surface saturation is a useful measure of the effectiveness of adsorption of surfactant at the liquid–gas or liquid–liquid interface, as it is the maximum value that adsorption can attain. The Γ_{\max} values were used for calculating the minimum area A_{\min} at the aqueous–air interface. The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecules, when compared with the dimensions of the molecule as obtained from models. From the surface excess concentration, the area per molecule at the interface is calculated using the equation: $A_{\min} = 10^{16}/N \Gamma_{\max}$; where N is Avogadro's number.²⁷ The Γ_{\max} and A_{\min} values were calculated and listed in Table I. It was observed that A_{\min} of GT-Pyr-Br cationic surfactant decreased as compared to GD-Pyr-Br cationic surfactants. This can be attrib-

uted to the fact that the cationic surfactants with more than hydrophilic groups pack more easily at the interface, thus obstructing the main chain interaction at the interface; this causes the molecule to occupy a smaller area.

The effectiveness of surface tension reduction, $\Pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$ (where γ_0 is the surface tension of water and γ_{CMC} is the surface tension of solution at CMC), was determined and listed in Table I. The effectiveness of surface tension reduction, Π_{CMC} , was increased for GT-Pyr-Br surfactant. The effectiveness of adsorption depends on the orientation of the surfactant at the interface and on the amount adsorbed at surface saturation. If the arrangement is predominantly perpendicular but not close-packed, there may be some increase in the effectiveness of adsorption with an increase in cationic group, resulting from greater Van der Waals attraction, and consequently yielding closer packing of longer chains.

Efficiency of adsorption, $P^{\text{C}20}$, is determined by the concentration (mol/dm^3) capable to suppress the surface tension by 20 mN/m. The efficiency of the prepared surfactants, listed in Table I, was increased for GT-Pyr-Br more than GD-Pyr-Br. This result indicates that GT-Pyr-Br surfactant is highly adsorbed at air/water interface more than GD-Pyr-Br surfactant.

Deinking of LDPE surface using the prepared surfactants

Effect of pH

The effect of pH on deinking of LDPE in the presence of GD-pyr-Br and GT-pyr-Br surfactant is represented in Figure 4(a,b) respectively. In this system, two different behaviors for deinking of LDPE were observed for the prepared surfactants at different pH levels. Figure 4(a) shows that GD-pyr-Br surfactant has only deinking effect at pH 12.5 and 13 (it was insoluble above pH 13 and below pH 12.5). It was found that the effectiveness of GD-pyr-Br surfactant at pH 12.5 was greater than that at pH 13. The percentage ink removed increased significantly as the surfactant concentration increased. It reached to 96% at the CMC of the surfactant at pH 12.5. Effectiveness of GT-pyr-Br surfactant was only found at pH range from 1 to 3, above this range the

TABLE I
CMC and Surface Activity Data of GT-Pyr-Br and GD-Pyr-Br Surfactants at 30°C

Characteristics	Units	GT-Pyr-Br	GD-Pyr-Br
CMC	mol/dm^3	0.035	0.125
Π_{CMC}	mN/m	41.7	43.9
γ_{CMC}	mN/m	30.5	28.3
$P^{\text{C}20}$	$-\log(\text{mol/dm}^3)$	5.7	5.45
$\Gamma_{\max} \times 10^{10}$	mol/cm^2	8.02	6.32
A_{\min}	nm^2	0.205	0.260

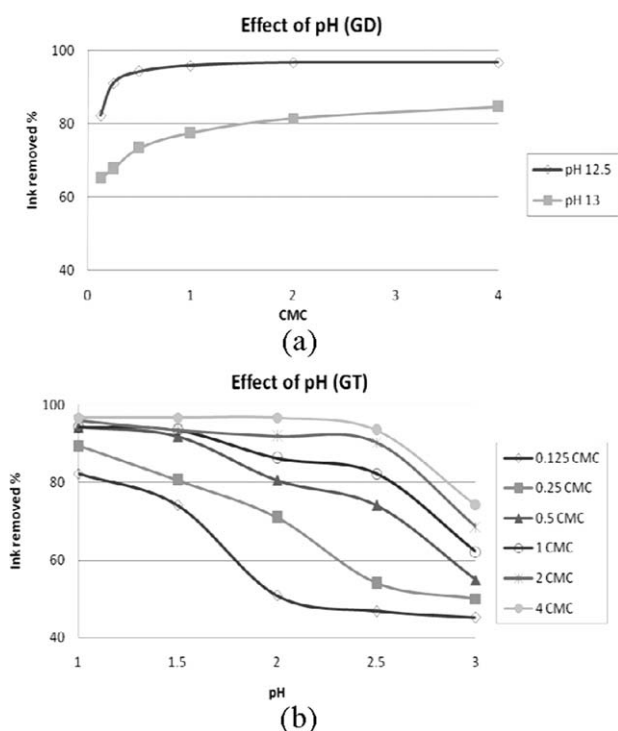


Figure 4 Effect of pH on the percentage ink removed from printed PE film at various surfactant concentrations of (a) GD-pyr-Br surfactant and (b) GT-pyr-Br surfactant, respectively, at 1 h shaking and 1 h soaking time.

surfactant did not show any solubility. Figure 4(b) shows that the percentage ink removed decreased as the pH increased from pH 1 to 3 and increased with increasing surfactant concentration. More than 90% of ink removal was attained at 0.5 CMC and above

at pH 1 and 1.5. No more than 74% of ink removal was observed at pH 3 along the whole range of CMC. It is well known that the vast majority of cationic surfactants are based on the nitrogen atom carrying the cationic charge. Both amine- and quaternary ammonium-based products are common. The amines only function as a surfactant in the protonated state; therefore, they cannot be used at high pH values. On the other hand, quaternary ammonium compounds are not pH sensitive. It is well known that the cationic surfactants have strong ability to adsorb at interfaces in acidic media. The positive charges in amines cationic surfactants are stable in acidic medium, and these surfactants lose their charges in alkaline medium.²⁸ Quaternary ammonium compounds, when treated with strong base, will undergo elimination reaction to yield the least substituted alkene.²⁹ Based on the results obtained in this work, the proposed mechanism for the removal of the solvent-based ink for LDPE surfaces at different pH level is based on surfactant adsorption and solubilization of surfactants and ink binder in micelles in acidic or basic media. It was also reported that the solubilization of ink binder in surfactant micelles is a very important step for deinking process. It has been hypothesized that the ink binder possesses negative charge which is the cause of the effectiveness of cationic surfactants relative to surfactants of another charges.²⁹ FTIR spectrum of the solvent-based ink binder is illustrated in Figure 5. The absorption band at 3418 cm^{-1} and 1720 cm^{-1} which attributed to NH and C=O stretching, respectively, can be referred to the presence of amide group in the chemical structure of the ink binder. The

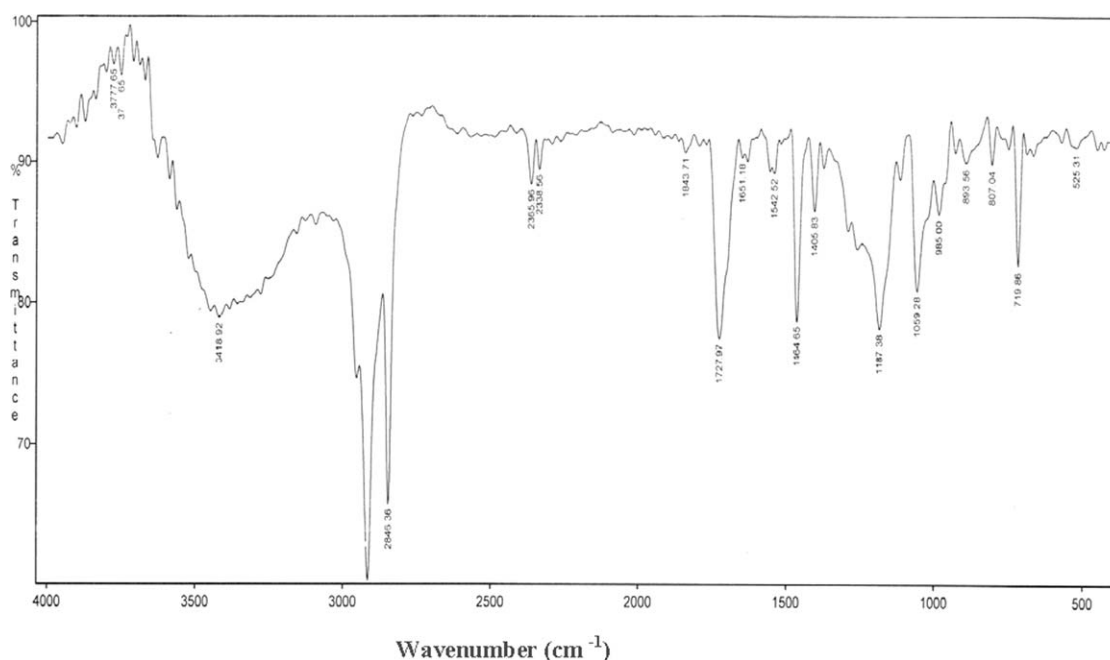


Figure 5 FTIR spectra of the solvent-based ink binder.

presence of medium bands at 1400 and 720 cm^{-1} can be attributed to C–N stretching and NH bending, respectively. The appearance of bands at 3050, 1650 and 810 cm^{-1} which attributed to aromatic CH stretching, C=C stretching and CH out of plan bending, respectively, indicates the incorporation of aromatic moieties in ink binder. Accordingly, it can be concluded that the solvent-based ink binder may be based on aromatic polyamide binder. Under both strong acidic and basic conditions, the amide group can be hydrolyzed to amine and acid. Under acidic condition, the amine will convert to amine salt which possesses positive charge on the PE surface. Under strong basic condition, the acid groups of the hydrolyzed polyamide ink resin will possess negative charge due to ionization of COOH to COO^- ionic moieties. Accordingly, it was expected that the deinking process can be increased at high pH due to association of cationic head groups of surfactants with negative moieties of polyamide via electrostatic interactions, thus enhancing the adsorption of cationic surfactant on the ink surfaces.²³ It is well known that the adsorption of cationic surfactant on the ink surface is deriving by both electrostatic and Van der Waals forces. On the other hand, pH does not affect the Van der Waals interactions between the hydrophobic part of surfactants and hydrophobic part of the pigment surfaces greatly. In addition, the Van der Waals interactions should increase with increasing the hydrophobic contents in the surfactant molecule. In this work, it was observed that the solubility of GT-pyr-Br surfactants increased in acidic medium. On the other hand, the solubility of GD-pyr-Br surfactant was increased in alkaline medium at pH more than 12. This behavior can be explained on the basis that GT oligomers have high amine content than GD oligomer which increases the tendency of GT-pyr-Br surfactants to protonate than GD-pyr-Br surfactant and, consequently, increases the solubility of GT-pyr-Br in acidic medium. In this work, both GD-py-Br and GT-pyr-Br as illustrated in Scheme 1, have the same hydrophilic head group and the difference is the contents of $\text{NCH}_2\text{—CH}_2\text{OCOCH}_2\text{Br}$ as hydrophobic tail. It was observed that the GT-pyr-Br surfactant contains more hydrophobic tail as side group and at the end of oligomer chains than GD-pyr-Br. On the other hand, the ability of GT-pyr-Br surfactant to protonate beside its ability to form quaternary amine increases its tendency to solubilize in acidic medium. Accordingly, the proposed mechanism for deinking of LDPE in the presence of GT-pyr-Br at low pH is based on high Van der Waals interaction between tail group of Gt-pyr-Br and hydrophobic part of the ink particles and interaction between dipole–dipole interaction between ester group or π - electrons of the aromatic ring of surfactants and amide groups or π - electrons of the aromatic ring of polyamide ink binder molecules solubilized in the palisade layer of the micelles. As the alkyl chain lengths

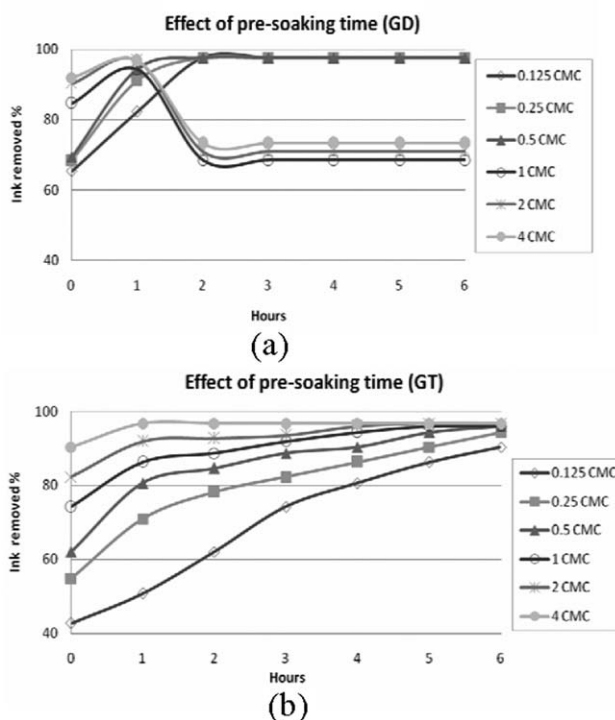


Figure 6 Effect of soaking time on the percentage ink removed from printed PE film at various surfactant concentrations of (a) GD-pyr-Br surfactant and (b) GT-pyr-Br surfactant, respectively, at 1 h shaking time.

and contents of the surfactant increased, the volume of the hydrophobic core increase as the micelle diameter increases, and increased micellar volume tends to increase solubilization due to hydrophobic bonding between surfactant and ink binder.³⁰ The adsorbed surfactant layer on pigment and polymer surface gives electrostatic stabilization of detached ink pigment. The electrostatic repulsion from the positively charged head groups of GT-py-Br molecules absorbing on both the detached ink and the LDPE surfaces can help to prevent the detached ink particles from redepositing on the LDPE surface. Solubilized binder molecules are unavailable for readsorbing or redeposition. On the other hand, the deinking effect GD-pyr-Br surfactant in alkaline medium can be illustrated on the basis of the electrostatic interaction between negative charges of polyamide ink binder and positive charge of cationic GD-pyr-Br surfactants as illustrated in Scheme 1. The mechanism of deinking process in the presence of cationic surfactants in alkaline medium was discussed.²³

Effect of soaking time

Figure 6(a,b) represents the effect of soaking time on the amount of ink removed from printed plastic film surface at various surfactant concentrations of GD-pyr-Br surfactant (pH 12.5) and GT-pyr-Br surfactant (pH 2), respectively, at 25°C and 1 h shaking time.

The figure shows that the presence of cationic surfactant has a significant effect in deinking process comparing with the deinking without surfactant. It was found that 22% of ink removed when using HCL solution (pH 2), whereas 12% ink removed in NaOH solution (pH 12.5) without surfactant as blank experiments at 1 h soaking and 1 h shaking.

The results showed also that the prepared surfactants behave differently during the deinking process. At 0.5 CMC and below of GD-pyr-Br surfactant, the amount of ink removed significantly increased as the soaking time was increased; the percentage ink removal reached 98% at 2 h soaking. At CMC and above, the percentage ink removed increased first by increasing the soaking time to 1 h then decreased. Above CMC, GD-pyr-Br surfactant became less effective at solubilization of ink binder so the amount of ink removed from plastic surface decreased.

The amount of ink removed significantly increased as the soaking time increased using GT-pyr-Br surfactant at all surfactant concentrations. At 0.125 CMC, the ink removal increased from 43 to 90% as soaking time increased from 0 to 6 h. At 0.5 CMC, the ink removal reached to 92% at 4 h of soaking time, whereas the amount of ink removal reached to 97% at 4 CMC and at 1 h of soaking time. The surfactant can aid detachment by mechanisms such as adsorption on ink and plastic surfaces decreasing ink/water and plastic/water interfacial tensions, making detachment more thermodynamically favorable. Above the CMC, the primary function of incremental surfactant is to solubilize ink molecules within micelles. A secondary advantage could be the micelles disassociating to provide surfactant monomer, speeding up rate-driven processes.³¹

Effect of shaking time

At the standard conditions of 1 h soaking time, pH 12.5, and at 25°C, the amount of ink removed increased as the shaking time and GD-pyr-Br surfactant concentration increased as shown in Figure 7(a). The amount of ink removing reached to 95% at 1.5 h of shaking time (and above). At 0.5 h, the effectiveness of the GD-pyr-Br at its CMC value and above was greater than that below CMC. The percentage of ink removal was 74–82 % at 1–4 CMC, while it was not exceeded 42% below CMC. Shaking process in presence of abrasives is an effective method for deinking of printed LDPE film, as the amount of ink removed after 1 h of soaking (at 0 shaking time) not exceeded 13%. The increase in the ink removal at concentrations greater than its CMC could be a result of the solubilization of ink components within the inner core of the micelles.²³ The percentage ink removed using GT-pyr-Br surfactant is illustrated in Figure 7(b). It is shown that at 0.125 CMC, the ink

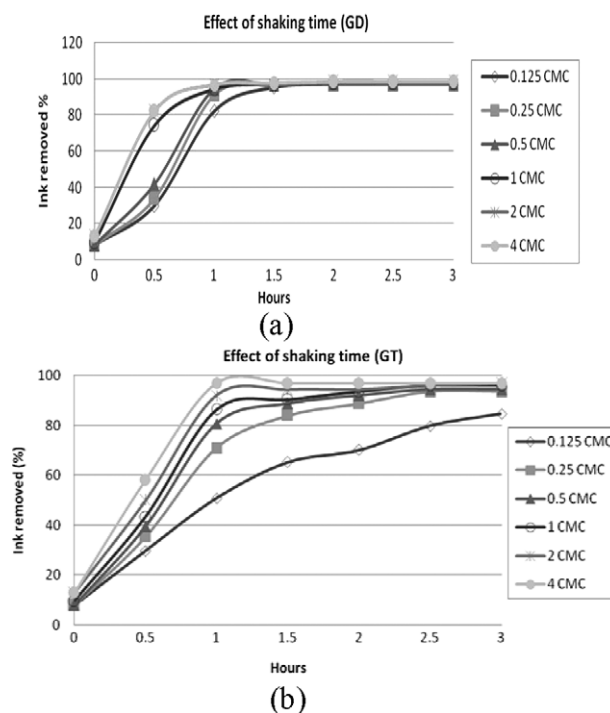


Figure 7 Effect of shaking time on the percentage ink removed from printed PE film at various surfactant concentrations, (a) GD-pyr-Br surfactant and (b) GT-pyr-Br surfactant, respectively, at 1 h soaking time.

removed increased from 8 to 85% as shaking time increased from 0 to 3 h. At CMC, 90% of ink removal was attained at 2 h of shaking time, whereas at 4 CMC the amount of ink removed reached to 97% at 1 h of shaking time. At CMC of GT-pyr-Br surfactant, 92% of ink removal was reached at shaking for 1 h and 3 h soaking time [Fig. 6(b)], while the same percentage was attained at 1.5 shaking time and 1 h soaking time. Longer soaking times permit shorter shaking times and longer shaking times permit shorter soaking times. Thus, soaking may improve deinking process economics. Since soaking is less expensive than agitated process units.³¹ Comparing the effect of 0.125 CMC of both GT-pyr-Br and GD-pyr-Br, at 1 h shaking and 1 h soaking time, it was found that 82% ink removal was attained in the case of GD-pyr-Br surfactant, while it was 51% only in the case of GT-pyr-Br. The same effect was found at higher concentrations. Thus, GD-pyr-Br surfactant has substantial deinking effect than GT-pyr-Br.

Deinking efficiency of the prepared surfactants

The deinking efficiency of the new cationic surfactants was confirmed by using the CIELAB (L^* , a^* , b^*) color scale. Figure 4(a) illustrates that the pH 12.5 of GD-pyr-Br surfactant solution is more effective in ink removing than pH 13. The total color

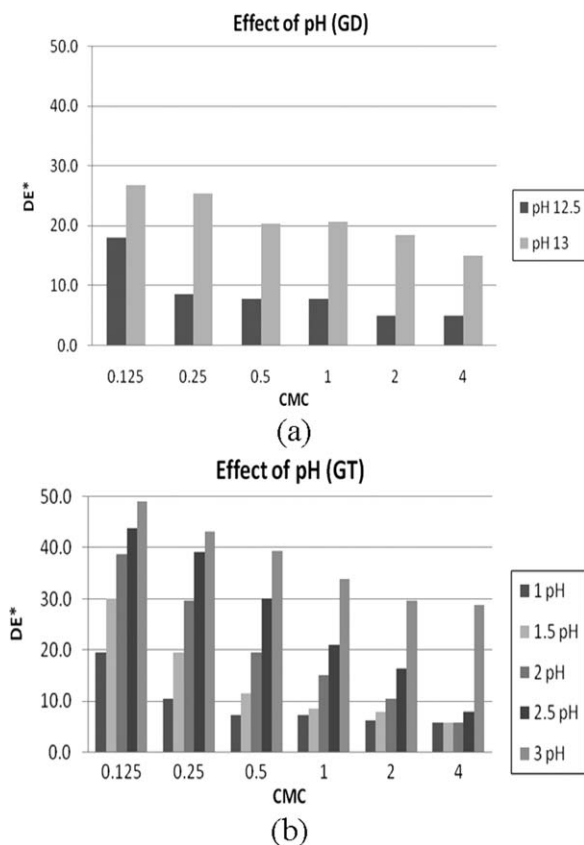


Figure 8 The total color difference DE^* between the standard (clear plastic film) and the deinked samples treated with (a) GD-pyr-Br surfactant and (b) GT-pyr-Br surfactant, respectively, as a function of pH.

difference DE^* decreased as the CMC was increased as shown in Figure 8(a). The decrease in DE^* value indicates a decrease in ink residue on plastic film, i.e., an increase in the amount of ink removed. This is consistent with the results observed in Figure 8(a). The total color difference DE^* increased as the pH was increased when using GT-pyr-Br surfactant, while it decreased as the surfactant concentration was increased [Fig. 8(b)]. The smallest amount of ink was removed at pH 3 because the solubility and efficiency of GT surfactant decreased at this pH (and above).

Figure 9(a,b) show the total color difference DE^* between the standard (clear plastic film) and the deinked samples treated with (a) GD-pyr-Br surfactant and (b) GT-pyr-Br surfactant, respectively, as a function of soaking time. It was observed that at 0 and 1 h of soaking time (1 h shaking time), DE^* decreased as the GD-pyr-Br surfactant concentration was increased, which means that the deinking efficiency was increased. Below the CMC, at 2–6 h of soaking time, DE^* has the lowest value (lower ink residue but higher ink removal). Above the CMC, higher ink residue at CMC which decreased as the CMC increased. The DE^* values were decreased as the

soaking time and the GT-pyr-Br surfactant concentration increased [Fig. 9(b)]. This result consistent with that obtained by measuring the % of ink removed [Fig. 6(b)].

The effect of shaking time on the total color difference DE^* between the standard (clear plastic film) and the deinked samples treated with GD-pyr-Br surfactant and GT-pyr-Br surfactant was represented in Figure 10(a,b), respectively. The total color difference DE^* has the highest value at zero shaking time in the case of GD-pyr-Br surfactant, i.e., the highest ink residue was observed at 0 shaking time as shown in Figure 10(a). The ink residue decreased as the shaking time was increased until it stabilized beyond 1 h of shaking time. This result is consistent with that observed in Figure 7(a). DE^* values decreased as the shaking time was increased in the case of GT-pyr-Br surfactant, which means that the amount of ink removed was increased. Shaking process is more effective in ink removing than soaking [Figs. 9(b) and 10(b)]. However, surfactants may be necessary to reduce the surface or interfacial tension at the air/water, ink/water, and plastic/water

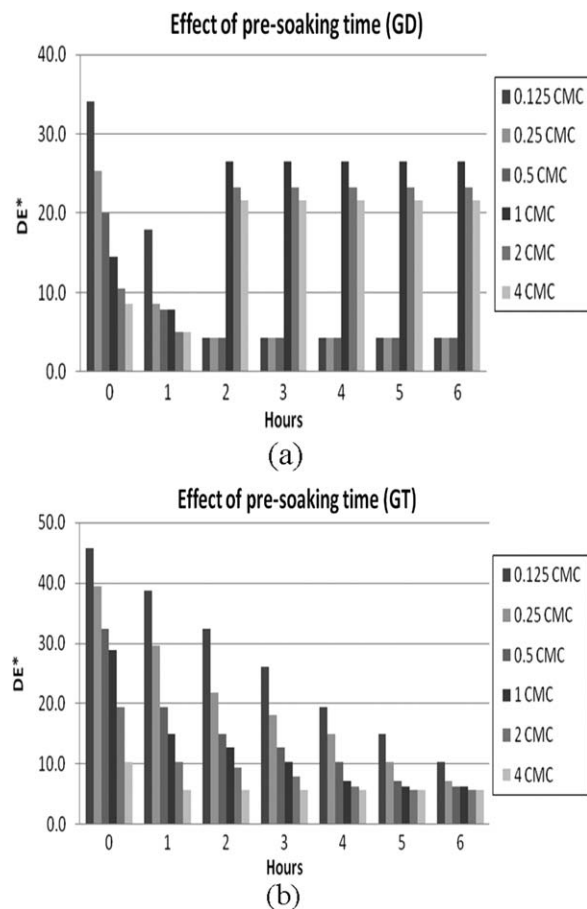


Figure 9 The total color difference DE^* between the standard (clear plastic film) and the deinked samples treated with (a) GD-pyr-Br surfactant and (b) GT-pyr-Br surfactant, respectively, as a function of soaking time.

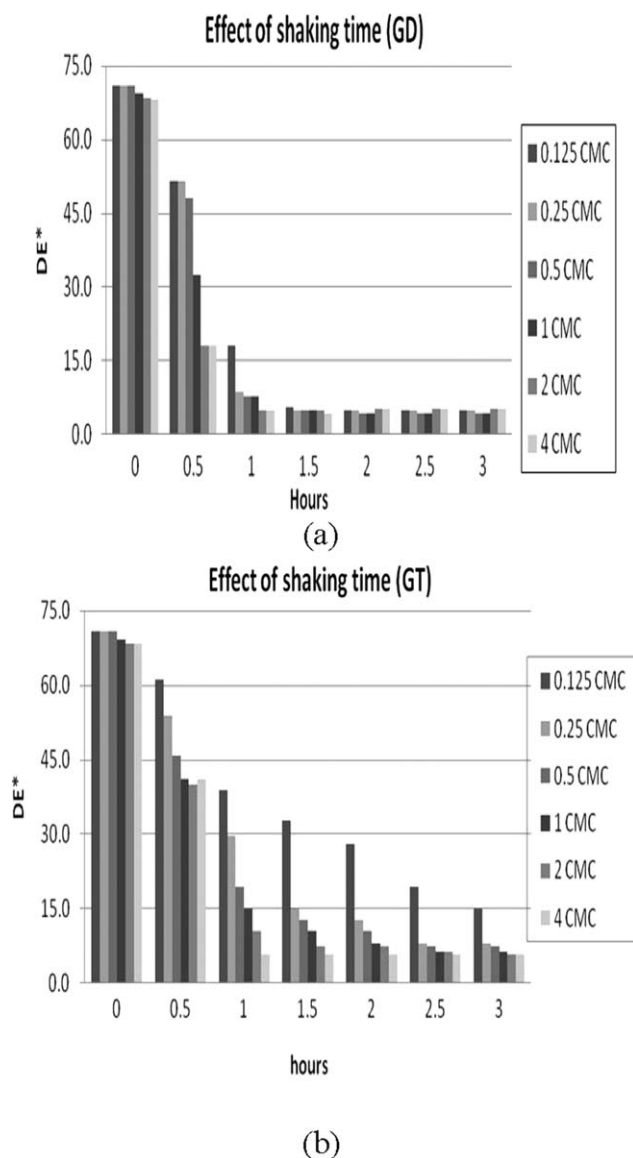


Figure 10 The total color difference DE^* between the standard (clear plastic film) and the deinked samples treated with (a) GD-pyr-Br surfactant and (b) GT-pyr-Br surfactant, respectively, as a function of shaking time.

interface, and this affects the wettability of the solution and facilitates the penetration of surfactant molecule between the ink particle and the plastic film.¹⁵

CONCLUSIONS

This work investigates the effects of pH, soaking time, and shaking time on the removal of solvent-based ink from LDPE surfaces based on the use of two new cationic surfactants, which prepared from PET waste. The prepared cationic surfactants behave differently in different pH media also their effectiveness in deinking process was different. GT-pyr-Br surfactant function well (solubilized) in acidic medium (pH 1–3), whereas GD-byr-Br surfactant func-

tion well in alkaline medium (at pH 12.5–13). GD-Pyr-Br surfactant possesses higher CMC value than GT-Pyr-Br, so it has higher solubility in water/ 2-propanol. This may also decrease the CMC values with increasing number of such groups substituted on the cationic sites. The result indicates that GT-Pyr-Br surfactant is highly adsorbed at air/water interface more than GD-Py-Br surfactant because the efficiency of the prepared surfactants was increased for GT-Pyr-Br more than GD-Pyr-Br. It was found that 22% of ink removed when using HCl solution (pH 2), whereas 12% ink removed in NaOH solution (pH 12.5) without surfactant as blank experiments at 1 h soaking and 1 h shaking.

GD-pyr-Br surfactant has only deinking effect at pH 12.5 and 13. It was found that the effectiveness of GD-pyr-Br surfactant at pH 12.5 was greater than that at pH 13. Effectiveness of GT-pyr-Br surfactant was only found at pH range from 1 to 3, more than 90% of ink removal was attained at 0.5 CMC and above at pH 1 and 1.5. No more than 74% of ink removal was observed at pH 3 along the whole range of CMC.

The amount of ink removing in the case of 0.125 CMC and above of GD-pyr-Br reached more than 80% at 1 h of shaking time, while it reached the same percentage after 1.5 h of shaking time at 0.25 CMC and above of GT-pyr-Br surfactant. Shaking process in presence of abrasives is an effective method for deinking of printed LDPE film, as the amount of ink removed after 1 h of soaking (at 0 shaking time) not exceeded 13%.

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