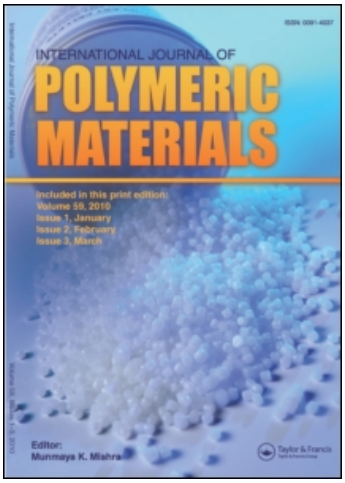

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Nonionic surfactants from poly(ethylene terephthalate) waste: I. Influence of structural variations on the surface activity

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Online publication date: 27 October 2010

To cite this Article Abdel-Azim, Abdel-Azim A. , Mekewi, Mohamed A. and Gouda, Shaban R.(2002) 'Nonionic surfactants from poly(ethylene terephthalate) waste: I. Influence of structural variations on the surface activity', International Journal of Polymeric Materials, 51: 9, 813 — 822
To link to this Article: DOI: 10.1080/714975837
URL: http://dx.doi.org/10.1080/714975837

International Journal of Polymeric Materials, 51:813–822, 2002

0091-4037/02 $12.00 + .00
DOI: 10.1080/00914030290046354

NONIONIC SURFACTANTS FROM POLY(ETHYLENE TEREPHTHALATE) WASTE: I. INFLUENCE OF STRUCTURAL VARIATIONS ON THE SURFACE ACTIVITY

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Poly(ethylene terephthalate), PET, waste was depolymerized with propylene glycol (PG) to an oligoester (OE). The hydroxyl value of the glycolized product before and after removing the free glycol were determined. The glycolized product was reacted with polyethylene glycol (PEG) of different molecular weights, namely, 600, 1000 and 4000 to form compounds having different hydrophil–lipophil balance (HLB) and hence different surface activities. The interfacial tension at the aqueous/benzene interface was determined. It was found that the demulsifiers' concentrations required to cause minimum interfacial tension are always less than that inducing maximum demulsification efficiency. The demulsification efficiency of the prepared surfactants in breaking synthetic water-in-benzene emulsions stabilized by petroleum asphaltenes was evaluated. The data revealed that the demulsification efficiency increases with increasing the demulsifiers' concentration, contact time and hydrophilicity.

Keywords: poly(ethylene terephthalate), recycling, glycolysis, demulsifier, propylene glycol, polyethylene glycol, asphaltenes

INTRODUCTION

The most common type of chemical degradation of polymers is hydrolysis-cleavage of a chemical bond with addition of a water molecule. The hydrolysis of some high-molecular-mass compounds is accelerated in the presence of natural catalysts, namely, enzymes, which act selectively on specific bonds. With increasing degree of degradation the proportion of end

Received 6 June 2000; in final form 8 June 2000.
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groups increases and their effect on the properties of the polymer becomes perceptible. Polyester hydrolysis can be used for regenerating the initial components from production wastes. Poly(ethylene terephthalate), PET, can be hydrolyzed with sulfuric acid and the resulting low-molecular polymer or mixture of monomers can be re-used for synthesizing the polyester. PET is synthesized from esters of the acid rather than from the free acid. Hence, it is more expedient to split up the wastes by alcoholysis (glycolysis) than hydrolysis. Thus, treatment of PET with boiling glycol results in diglycolic ester of terephthalic acid or a low-molecular polyester with glycolic end groups [1, 2], which can again take part in condensation or polycondensation reaction [1 – 4].

Dispersion of a liquid phase into another relatively immiscible phase frequently occurs in operations involving liquid – liquid contacting. Some of these dispersions are desirable, as in the food and cosmetic industry, while there are many situations where such dispersions, or emulsions, are undesirable as in the petroleum industry [5].

Petroleum emulsions are mainly water-in-oil type, in which the oil constitutes the continuos phase, while water or water having various mineral salts dissolved therein constitutes the dispersed phase [6].

Unlike other techniques, chemical demulsification has the great advantage of being able to break an emulsion *in situ*. Demulsifiers are all polymeric surfactants capable of being adsorbed at the oil/water interface and displacing the interfacial film formed therein [7 – 9]. Asphaltenes in the oil possess a sufficient number of functional groups to penetrate the oil/water interface and form an interfacial layer of great mechanical strength [10]. Demulsification can take place only when the interfacial layer is broken by an agent whose surface activity is superior to that of the asphaltenes [11].

Synthetic water-in-oil emulsions were utilized by several authors [12 – 17] to simulate water-in-crude oil natural emulsions. This simulation was utilized to overcome the various uncontrollable variables [18] of natural emulsions. Some of these variables are: the percentage of asphaltenes, percentage of water or brine, percentage of salt and their chemical constitution and the thermal history [19]. All these variables can't be controlled since they change drastically from one batch to another and they cause a great confusion for the proper scientific study [20].

The present investigation pertains to:

- synthesize a series of nonionic polymeric surfactants based on polyoxyethylenated glycolized product of PET (POGP) to be used as water-in-oil emulsion breakers;
- test the capability of the prepared polymeric compounds in reducing the oil/water interfacial tension (IFT);

- study the effect of molecular weight of the hydrophilic moiety and the hydrophil–lipophil balance (HLB) of the prepared polymeric compounds on their demulsification potency; and
- study the effect of the degree of salinity and the pH value of the aqueous phase on the demulsification efficiency of the prepared polymeric compounds.

In this respect water-in-benzene synthetic emulsions stabilized by asphaltenes will be used to simulate naturally occurring water-in-crude oil emulsions.

EXPERIMENTAL

Converting Poly(ethylene terephthalate) Waste to GP

The PET waste (beverage bottles) was depolymerized using propylene glycol (PG) in presence of manganese acetate as a trans-esterification catalyst. The concentration of the catalyst was 0.5% (by weight) based on the weight of the PET while the weight of the glycol mixture used for glycolysis was 65% of the weight of PET. The reaction was carried out at temperature about 200°C under reflux for 4 h in nitrogen atmosphere, and at 210°–230°C for 3 h. The temperature of the reaction system was then allowed to drop to 100°C and maintained at this temperature for 1 h. The temperature was then allowed to drop to room temperature. The glycolized product was then analyzed for hydroxyl value and the amount of free glycols. The hydroxyl values were determined by the conventional acetic anhydride/pyridine method [21]. In order to determine the amount of the free glycol, a weighed quantity of the glycolized product was extracted with water and filtered. The aqueous filtrate containing free glycol and some water-soluble oligomers was concentrated by evaporation of water. The water-soluble oligomers were separated by precipitation from the free glycol by cooling the filtrate. The precipitated water-soluble oligomers were filtered and added to the residue remaining after the first filtration and weighed together. The difference between the initial and the final weights represents the amount of free glycol removed by water extraction.

Ethoxylation of OE Using *b,b′*-dichloro Diethyl Ether and Polyethylene Glycol

Three different molecular weights of polyethylene glycol (PEG) were used, namely, PEG 600, 1000 and 4000 to produce the demulsifiers Dl, D2 and D3, respectively. The procedure described in Ref. [22] was used for synthesis of *b,b′*-dichloro diethyl ether.

In a 250 ml Three necked round bottom flask, fitted with condenser, mechanical stirrer and thermometer were added 0.1 mole GP, 0.2 mole

TABLE 1 Specifications of the synthesized POGP

Designation	*M. wt. of PEG*	*HLB*	*PC*	*Theoretical M. wt.*
D1	600	12.50	3.44	1922
D2	1000	14.70	28.24	2722
D3	4000	18.39	91.98	8722

β,β'-dichloro diethyl ether, 0.2 mole PEG and 0.4 mole NaOH. The reactants were agitated and slowly heated to a temperature of 170°C. The reaction mixture was maintained at this temperature for 5 hr.

The progress of the reaction was followed by determining the NaCl content which increases gradually to reach a constant value at the end of the reaction. The product was then treated with an equal volume of saturated NaCl solution, neutralized with dilute HCl. The temperature of the mixture was then raised to 90°C and maintained for one hour. The upper waxy layer was separated and dried in vacuum oven at 50°C to a constant weight. Demulsifiers with different molecular weights and HLB were obtained by varying the molecular weights of PEG. The characteristics of the prepared compounds and their designations are listed in Table 1.

Interfacial Tension Measurements

Spinning drop interfacial tensiometer, Model Kruss Site-04, was used for measuring the interfacial tension between surfactants' aqueous solutions and benzene as an oil phase for which the elongation of the injected drop in the capillary was measured at an adjusted temperature (25°C) and speed of rotation. The interfacial tension (g) was calculated from the following equation:

$$\gamma = 3.427 \times 10^{-7}(0.17\delta)^3 \times n^2 \times \Delta\rho$$

where δ, n and $\Delta\rho$ are the diameter of the drop, the speed of rotation and the density difference between the oil phase and the surfactant aqueous solution, respectively.

Determination of the Partition Coefficient (PC) for the Prepared Polymeric Demulsifiers

The partition coefficient expressed as the ratio of the solubility of a surfactant in the aqueous phase to its solubility in the oil phase was determined quantitatively by UV absorbance technique. The details of the preparation of the test samples and the construction of the calibration curves were described in our previous publication [12].

Preparation of Asphaltenes Stabilized Water-in-Benzene Synthetic Emulsions

Asphaltenes were separated from Land Belayim crude oil (containing 8% asphaltenes). The procedure described by the standard method of the Institute of Petroleum (IP 143/84) was followed for precipitation of asphaltenes by *n*-heptane. Stabilized water-in-benzene synthetic emulsion was prepared by homogenizing 20 ml of water (20 vol.%) and benzene (80 vol.%) containing 0.25 wt.-% asphaltenes. The emulsion was generated by sonication with an ultrasonic processor (model VCX 600, Sonics & Materials Inc., USA) for 30 seconds at room temperature.

Bottle Testing for Determining the Demulsification Capability of the Prepared POGP

The bottle test is used to estimate the capability of demulsifiers in breaking of water-in oil emulsions. Simulated synthetic emulsions (prepared as indicated in preceding section) were utilized for bottle testing. Different concentrations of the demulsifiers (ranging from 100 ppm to 500 ppm) were utilized. A graduated cone shaped tube (100 ml capacity fitted with teflon lid) was used to measure the separated water in each case. The amounts of separated water, at 35°C, were registered for each concentration at specific time intervals, namely, 0.5, 1, 2, 3, 4, 5, 6 and 24 hours. In all experiments, a blank was utilized for comparing the separated water in absence of the demulsifier due to the influence of temperature.

RESULTS AND DISCUSSION

Preparation and Characterization of the Glycolized Product

The glycolized product was obtained by reacting PET with PG. The weight ratio of glycol to PET waste was 0.65.

The free glycol in the glycolized product was measured according to the procedure described in the experimental section. The hydroxyl number before and after removing the free glycol were found to be 804 and 295 mg KOH/g, respectively. The measured value of free glycol (96% of the total volume of the glycol used) indicates that only about 4% of the glycol is used up in the trans-esterification. This finding runs in harmony with that found in a previous publication [3]. The hydroxyl number after removing the free glycol indicates that the extent of depolymerization is considerable and the glycolized product is mainly terminated with hydroxyl groups. Based on the obtained value of the hydroxyl number after removing the free glycol and the ^{1}HNMR study carried out by Tong *et al.* [4], the following monomer,

dimer and trimer compounds exist (Scheme 1):

$$HO\text{-}R\text{-}O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}R\text{-}OH$$

$$HO\text{-}R\text{-}O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}(CH_2)_2\,O\text{-}CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}R\text{-}OH$$

$$HO\text{-}R\text{-}O\text{-}(CO\text{-}C_6H_4\text{-}CO\text{-}O\text{-}CH_2CH_2\text{-}O)_2\text{-}C\,O\text{-}C_6H_4\text{-}CO\text{-}O\text{-}R\text{-}OH$$

SCHEME 1

In these formulae R is $HC(CH_3)CH_2$.

The glycolized product was reacted with three different molecular weights of polyethylene glycol (PEG), namely, PEG 600, 1000 and 4000 to produce the demulsifiers D1, D2 and D3, respectively.

The effect of surfactant's concentration on the IFT between benzene/water interface has been thoroughly investigated. For the three polymeric surfactants, the IFT was measured as a function of concentration at 25°C. The IFT- concentration isotherms (not presented here for brevity) show that the IFT decreases to attain certain value and then it remains constant no matter the concentration increases of the surfactant. The molar concentrations that induce the minimum IFT for D1, D2 and D3 were found to be 5.4×10^{-5}, 4.8×10^{-5} and 1.9×10^{-5}, respectively. The molecular weight of these polymeric surfactants are listed in Table 1. It can be seen that the increase in molecular weight is associated with a reduction in the number of molecules required for monolayer coverage of the benzene/water interface.

The prepared demulsifiers were designed in such a way to vary the HLB and molecular weight to investigate the influence of these variations on the demulsification efficiency of the synthesized surfactants. Synthetic water/benzene emulsions, stabilized by asphaltenes were prepared and used for testing the demulsification efficiency of the demulsifiers under investigation. The standard bottle test was utilized for testing the effect of demulsifiers concentration and the contact time on the demulsification efficiency (expressed as % coalescence). The measured values are listed in Table 2. Careful inspection of the data in this table reveals that, in all cases, the demulsification efficiency increases with increasing contact time. With respect to the effect of concentration on demulsification efficiency, it can be seen that maximum demulsification for the demulsifiers D1, D2 and D3 is attained at concentrations 500 ppm (2.60×10^{-4} M), 400 ppm (1.47×10^{-4} M) and 300 ppm (3.43×10^{-5} M), respectively.

TABLE 2 Demulsification efficiency expressed as % coalescence at different times (hr) and different concentrations (ppm) of the prepared demulsifiers

	Conc.	*% Coalescence at different times (hr)*							
Code	*(ppm)*	0.5	1.0	2.0	3.0	4.0	5.0	6.0	24.0
	100	10.1	10.1	11.8	13.7	16.0	19.2	19.2	26.4
	200	28.8	29.0	31.0	31.0	31.0	34.6	34.6	43.5
D1	300	34.2	35.1	38.2	39.7	39.7	41.5	41.5	46.0
	400	36.2	39.1	39.8	44.2	44.9	48.2	51.1	55.8
	500	41.0	41.1	45.8	45.8	47.7	47.8	49.0	57.9
	100	19.3	30.2	36.6	38.8	41.1	41.9	46.6	51.2
	200	34.5	36.8	38.2	42.5	42.7	46.2	51.1	59.3
D2	300	37.5	45.8	47.9	50.1	50.2	57.9	58.1	63.9
	400	43.2	47.1	45.2	62.9	63.2	66.1	69.0	74.2
	500	41.0	41.0	44.1	45.1	47.8	50.8	54.1	70.0
	100	19.6	32.1	36.8	38.8	42.0	43.4	44.9	54.7
	200	35.0	37.1	38.3	43.0	43.4	47.5	52.7	62.1
D3	300	47.8	58.5	65.5	65.9	85.9	86.6	90.0	99.0
	400	45.7	57.0	64.2	64.0	84.2	85.8	86.1	90.0
	500	41.1	41.2	46.8	47.7	54.1	52.2	54.9	66.2

It is obvious that, the molar concentration required to reduce the IFT to a minimum value is always less than that favorable to maximum demulsification. This may be explained by the fact that the IFT reduction occurs due to the monolayer adsorption at the benzene-water interface while the demulsification requires an extra number of demulsifier's molecules to dissolute asphaltenes [23]. As shown in Table 2, when the demulsifiers' concentration exceeds a certain value (400 ppm for D2 & 300 ppm for D3) the demulsification efficiency decreases. This phenomenon may be explained by the formation of a stable barrier formed by the demulsifier molecules clustering at the interface [24] which lead to a cessation of coalescence.

Effect of HLB of the Demulsifiers on Their Demulsification Efficiency

The HLB concept, firstly introduced by Griffin [25], is normally used as an important parameter to predict the action of the emulsifiers for a certain water – oil emulsion [26]. However, this concept has not been used extensively by scientists working in the field of demulsifiers. In the present study, the HLB value of the POGP was varied by altering the molecular weight of the PEG used as hydrophilic moieties.

The HLB values were calculated by Griffin's equation as follows:

$$\mathrm{HLB} = \frac{\%\ \text{ethoxylation}}{5}$$

The calculated values of HLB and the measured PC values for the polymeric demulsifiers under investigation are listed in Table 1. It can be seen that the HLB of the surfactants increases with increasing the number of ethylene oxide units. The same dependence is applicable on the PC values. Accordingly, it is obvious that the HLB is directly proportional to the PC.

For the sake of testing the effect of the HLB on the demulsification efficiency, it is desired to recall the data present in Table 2. It can be seen that the maximum % coalescence after 24 hours for D1, D2 and D3 are 57.9, 70.0 and 99.0, respectively, at concentrations 500 ppm, 400 ppm and 300 ppm for D1, D2 and D3, respectively. These data reveal that the amount of water separated increases with increasing the HLB and PC. This finding may be explained by either of the following speculations:

(1) The increase in the HLB value increases the solubility of the surfactant in the aqueous phase (dispersed phase). When the demulsifier is initially introduced to the water-in-oil emulsion, it will be more thermodynamically stable at the interface of the water droplets. Accordingly, the surfactants possessing high HLB migrate faster to the interface than those having low HLB. As a result of such enhanced migration toward the interface, the surfactant forms continuous hydrophilic pathways [24] between the dispersed water droplets. This leads to a rupture of the asphaltenes' interfacial film surrounding the water droplets.
(2) The enhanced demulsification efficiency of the more hydrophilic surfactants is based on the study accomplished by Eley *et al.* [27] and Laurence and Killner [28]. They stated that the destabilization of water-in-oil emulsions can be achieved by the addition of surface active agents which promote oil-in-water emulsions. It is well known that water soluble surfactants are more capable of stabilizing oil-in-water emulsions and *vice versa* [29]. The present work deals with a water-in-oil emulsion and hence it is clear that the higher the HLB and PC the higher the demulsification efficiency.

Cooper *et al.* [30] have found that demulsifiers embracing HLB ranging between 15 and 20 are considered the most effective in breaking water-in-oil emulsions. The present results confirm Cooper's finding since the investigated demulsifires' HLB lie in the HLB range recommended by Cooper.

CONCLUSIONS

Based on the experimental results the following conclusions are reached:

- The prepared POGP were found to have demulsification efficiency for breaking water – in – benzene synthetic emulsions stabilized by

asphaltenes. The demulsification efficiency increases by increasing the concentration of the investigated polymeric demulsifiers.

- The demulsification efficiency of D2 and D3 attained its highest value at concentrations of 400 ppm and 300 ppm, respectively and when the concentrations exceed these values, the demulsification efficiency decreases due to the clustering of the demulsifiers' molecules at the interface.
- The demulsifiers' concentrations required to cause minimum interfacial tension are always less than those inducing maximum demulsification efficiency. This was attributed to the consumption of the extra demulsifiers in dissolution of asphaltenes.
- the demulsification efficiency increases with increasing the contact time, and molecular weight & hydrophilicity of the demulsifier.

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