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Deinking of Polyethylene Terephthalate Film Using Surfactant

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Abstract
Polyethylene terephthalate (PET) is a commercial engineering polyester thermoplastic that is frequently used as a base film layer that bridges heat from the printerhead to the ink layer for thermal transfer ribbon application. This polymer is regarded as one of the best base materials for film since it portrays a good heat resistance and low shrinkage under high temperatures. However, continuous production of PET in the manufacturing sector has resulted in a drawback where cost becomes an issue. This study, therefore, emphasizes the importance of resolving the problem by recycling it while maintaining the properties through a deinking approach employing various surfactants under multiple conditions. During the process, PET sample collected from Dai Nippon Printing Co., Ltd. (DNP) was initially characterized by thermogravimetric analysis (TGA) for thermal stability and attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR) technique to obtain the list of functional groups within it. The sample was then treated with anionic and cationic surfactants: sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB), respectively, at different critical micelle concentrations (CMC), temperatures, and pH levels. After that, the sample was characterized by the ATR-FTIR method to compare the changes in functional groups following the deinking procedure. As part of this study, the physical appearance of the sample was also examined using the Brother iPrint & Scan and MatlabR2017b software, both before and after deinking, to see noticeable differences in the black ink's number of pixels. There was a distinct ink reduction percentage when surfactants were set above critical micelle concentration (CMC), high temperature, and strong basic environments. The PET sample immersed in SDS solution (5xCMC, 40°C) and (5xCMC, pH 12) recorded values of 99.29% and 100.00%, respectively, for ink removal percentage while CTAB with the same conditions were 99.98% and 100.00%. Hence, based on the results obtained, it can be deduced that CTAB is the excellent choice for deinking PET thermal transfer ribbon when paired with such optimum parameters.
Keywords: Polyethylene terephthalate (PET); Recycling; Deinking; Surfactants; Critical Micelle Concentration (CMC)

1. Introduction

Polyethylene terephthalate (PET) is a semicrystalline thermoplastic resin widely available on the market. Over the last 20 years, the use of PET has increased at the fastest rate compared to other types of plastic packaging. It is predicted that by 2030, global demand for PET will amount to 42 million metric tons (Tiseo, I., 2021). With the high consumption of this commercially popular polymer in the manufacturing sector, the challenges of supplying PET have become more difficult to tackle, given the high cost of the production process. As a result, many businesses are likely to consider recycling the used polymer to save the budget.

Previously, it was claimed that the physical and mechanical properties of recycled plastics were matchless to those of virgin plastics (Schyns, Z. O. G., & Shaver, M. P., 2021). One factor that causes property impairment such as loss of strength and stiffness is the ink commonly present on the plastic surface. Regardless, if the ink is removed, the physical properties of the recycled polymer can be preserved, akin to those of a pure one (Gecol, H. et al., 2002).

Thus, this study proposes a credible way to significantly enhance the ink removal method by employing surfactants in conjunction with several parameters applied during the process. These include the critical micelle concentration (CMC) of the surfactants, pH, and temperature. The sample will be

characterized before and after analysis using thermogravimetric analysis (TGA) for thermal stability and attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR), and optical scanning method to ensure that the hypothesis is valid. During the analysis, the PET films will be treated with two main types of surfactants: anionic (SDS) and cationic (CTAB). This is the first study to detail the three measurable factors that define PET film deinking using multiple surfactants.

This research aims to (1) characterize the polyethylene terephthalate (PET) film before and after the removal of ink (2) study the effect of different type of surfactants on the removal of ink on PET film (3) study the effect of different type of parameters used during the removal of ink on PET film.

2. Methodology

2.1 Chemical Characterization by TGA and ATR-FTIR

The TGA Q500 V20.13 Build 39, a model from TA Instruments GA was implemented in the study as it measured the sample's thermal stability and compositions from the observed weight change. Meanwhile, the Perkin Elmer ATR-FTIR Spectrometer was used to analyse the PET film before and after the deinking process for common functional groups available within the ink.

2.2 Preparation of the Surfactant's Solution

In the beginning, all glassware was cleaned with a standard lab detergent and then acid washed with a chromic acid solution (H_2CrO_4) for at least one hour. The surfactant solutions were prepared fresh with double deionized water as a precaution against contamination for each experiment. CTAB and SDS solutions were prepared by dissolving the respective solids with distilled water with continuous stirring from a magnetic stirrer to ensure they were homogeneous. A control sample was also prepared and tested with the surfactant solutions to maintain control over parameters such as pH and temperature. Each experiment was replicated twice for each parameter.

2.2.1 Concentration

The critical micelle concentration (CMC) values for the surfactant used were obtained from the National Standard Reference Data System (NSRDS) of the National Bureau of Standards for Critical Micelle Concentrations of Aqueous Surfactant Systems (Mukerjee, P. et al., 1971; Holmberg, K. (2019).

They were based on the surface tension log plot method for CTAB and surface tension linear plot method for SDS. Both were executed at 25°C without any added additives.

Table 1. Values of surfactants' concentration at different CMC levels

Surfactant	**Concentration**		
	CMC Value (M)	**Below CMC (M)**	**Above CMC (M)**
		25% of CMC	**5xCMC**
CTAB	9.20×10^{-4}	2.30×10^{-4}	4.60×10^{-3}
SDS	8.30×10^{-3}	2.08×10^{-3}	4.15×10^{-2}

Two requisite formulas have been applied to compute the mass of solid required for making these solutions at the respective concentration are:

$$c = \frac{n}{V} \quad (1)$$

where c is the molar concentration (M)
n is the number of moles (mol)
V is the volume (L); and

$$m = n \times M \quad (2)$$

where m is the mass of substance (g)
n is the number of moles (mol)
M is the molar mass of substance ($gmol^{-1}$)

Table 2. Mass of solid needed for the preparation of the surfactants

Surfac-tant	Concentrati-on	Molarity (M)	Volume (L)	No. of Moles (mol)	Molar Mass ($gmol^{-1}$)	Mass of solid (g)
	25% of CMC	$2.30x10^{-4}$		$2.30x10^{-5}$		$8.40x10^{-3}$
CTAB	CMC	$9.20x10^{-4}$		$9.20x10^{-5}$	364.45	$3.35x10^{-2}$
	5xCMC	$4.60x10^{-3}$	0.100	$4.60x10^{-4}$		$1.68x10^{-1}$
	25% of CMC	$2.08x10^{-3}$		$2.08x10^{-4}$		$6.06x10^{-2}$
SDS	CMC	$8.30x10^{-3}$		$8.30x10^{-4}$	288.38	$2.39x10^{-1}$
	5xCMC	$4.15x10^{-2}$		$4.15x10^{-3}$		$1.20x10^{0}$

2.2.2 pH

By using a dropper, 0.1 M of sodium hydroxide (NaOH) or 0.1 M hydrochloric acid (HCl) was dispensed drop by drop into the surfactant solution. Careful addition of these base and acid was necessary to adjust and maintain pH at the desired values. The portable Thermo Fisher Eutech pH 700 Electrochemistry Meter equipped with an open-pore pH electrode and an ATC probe was utilized to perform the pH measurements throughout the process.

2.2.3 Heating of Solution

Beakers containing solutions of various surfactants and concentrations were submerged in a controlled water bath, and the temperature of the water bath was adjusted so that each beaker was heated to one of three different temperatures ranging from 30 to 40°C.

2.3 Deinking of PET Film

2.3.1 Effect of pH

After obtaining the desired pH through the adjustment of 0.1 M NaOH and HCl, a cut PET sample was immersed in each surfactant class at varying concentrations for one hour while being continuously stirred. The sample was then evaluated for changes in response to the conditioned pH of 11, 11.5, and 12.

2.3.2 Effect of Temperature

To accelerate the dissolution of ink, the two types of surfactant solutions were slightly warmed to various temperatures: 30°C, 35°C, and 40°C. Once the target temperature was reached, the PET sample was immersed in them for one hour to observe the differences in the sample's state.

2.4 Analysis of the Deinked PET Film

Each deinked film sample was collected and visually evaluated based on the parameters tested. The deinked PET samples were characterized using attenuated total reflection Fourier transformed infrared spectroscopy (ATR-FTIR) in the same way as the original sample to compare and identify the functional groups available following the deinking process. Then, the Brother iPrint & Scan was utilized to determine the ink removal percentage. The scanning procedures were identical to the ones done on the initial sample. The image file was later imported into the MatlabR2017b software to obtain the histogram equalization and quantify the number of black ink pixels presented.

3. Results and Discussions

3.1 Chemical Characterization of PET Film

3.1.1 Thermal Stability

The 1.0150 mg sample was heated from ambient temperature to 1000°C in an inert nitrogen atmosphere at a controlled heating rate of 0.01°C/min by the TGA Q500 V20.13 Build 39 instrument.

As a result, the thermogravimetric analysis of the PET sample revealed a four-stage decomposition. At 122.34°C, the first weight loss of 11.66% was observed due to some volatile

substances present during the film's synthesis. These could be additives like plasticizers or mineral and carbon fillers. The purpose of adding such materials was to improve the film's physical properties, including heat resistance, deflection, and thermal expansion. Besides, the initial degradation could also correspond to the driving out of moisture and volatile solvents such as alcohols, ketones, and esters which made up the black ink.

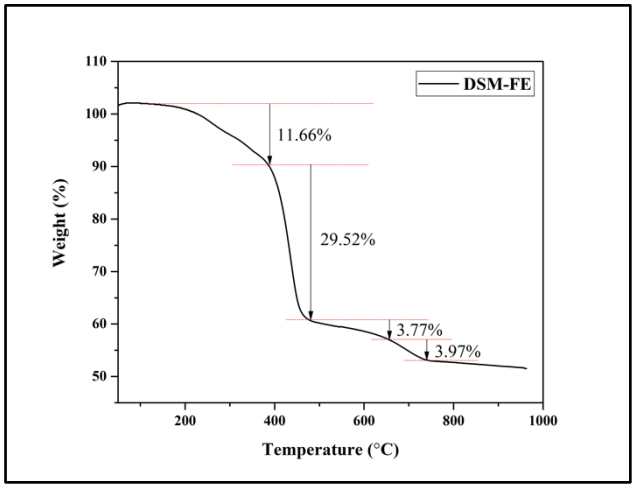

Figure 1. The TGA thermogram of the PET sample

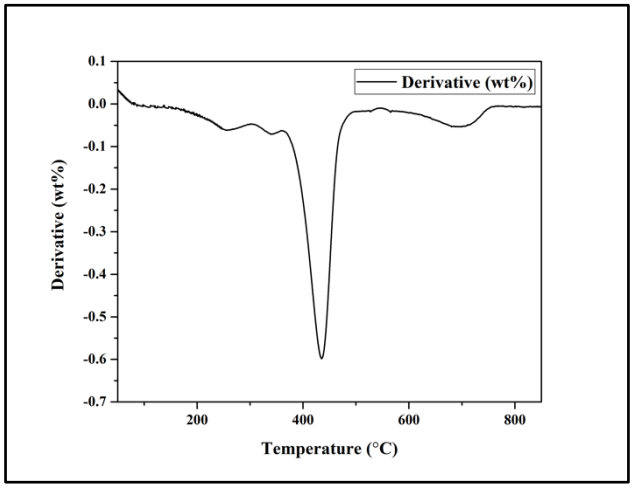

Figure 2. The derivative TGA thermogram of PET sample

The second weight loss was 29.52%, and it was thought endothermically occurred because of the rupture of diethylene glycol ($C_4H_{10}O_3$) via ester link random scission at 385.51°C. At 654.96°C and 740.30°C, the degradation of cross-linked carbonaceous structures took place with the total of weight loss of 3.77% and 3.97%, respectively (Miandad, R. et al., 2019). After the weight loss series, the solid PET sample continued decomposing smoothly until 963°C, at which no appreciable decomposition reaction was presented.

3.1.2 Functional Groups

ATR-FTIR measurement was performed in this study to identify the functional groups available on the PET black ribbon sample. Figure 3 depicted the ATR spectra of the sample prior to the deinking process and bands common to many compounds typically used in ink formulations. Intermolecular and intramolecular O-H bonds detected at 3543.55 cm^{-1}, 3428.31 cm^{-1}, and 3317.80 cm^{-1} were associated with the water and alcohol solvents common for many ink systems. On the other hand, the weak intensity N-H bands found at 3317.80 cm^{-1} and 1580.95 cm^{-1} corresponded to the presence of amine compounds utilized in producing black-colored ink. Small absorbance bands at 2906.41 cm^{-1} and 2107.40 cm^{-1} were also observed, ascribed to the vibrational stretching of C-H aliphatic hydrocarbon

and C≡C, respectively. Scanning through the spectra, the strong absorbance band was noticed and centered at 1712.03 cm^{-1}. The band indicated either C=O aliphatic ketone or carboxylic acid. Finally, multiple vibrational bands that constituted the ink were detected within the fingerprint region of 1700 cm^{-1} to 1000 cm^{-1}. They included C=C stretching, N-O stretching, S=O stretching, C-N stretching, and C-O stretching.

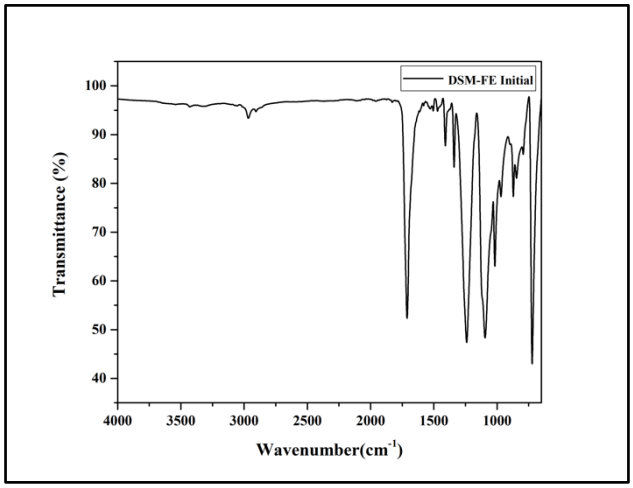

Figure 3. The ATR-FTIR spectra of PET sample

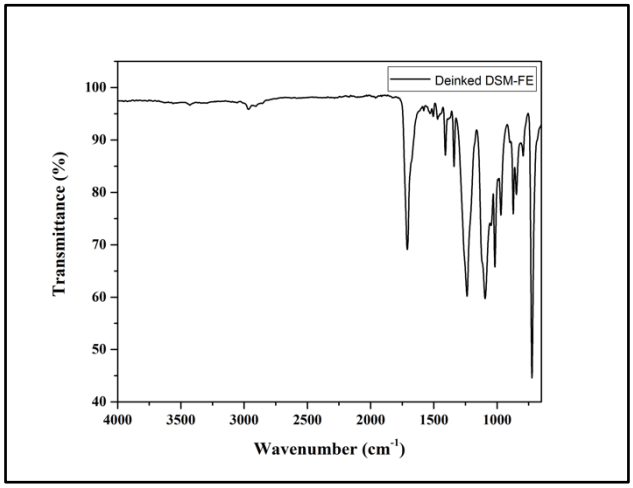

Figure 4. The ATR-FTIR spectra of deinked PET sample

When the cationic and anionic surfactants were added for ink removal, the intensity of the sample's spectra became much lower and noticeable functional groups detachment were observed like intermolecular and intramolecular O-H, N-H, C≡C, and C=C.

3.2 Effect of Concentration and pH on Deinking of PET Film

Testing has been done on the pH parameter to ensure that an ideal environment was created for efficient ink removal. For this study, each surfactant was prepared with three distinct concentrations placed below, during, and above the critical micelle concentration (CMC) and at pH of 11, 11.5, and 12. The PET sample demonstrated an increasing tendency toward deinking in a more concentrated and basic environment. For both CTAB and SDS, the ink removal percentage happened to be 100% at such conditions. However, there was a slight difference in deinking rate as visually proven in Table 4.

When the ribbon was submerged in a basic solution, the carboxylic groups of the ink would deprotonate and form carboxylate ions. The hydrophilic cationic head of the surfactant added would attach to these anionic ions through electrostatic interaction. In contrast, its hydrophobic anionic tail remained attached to other anionic tails and away from water. As the ribbon's surface became saturated

with the surfactant, its hydrophilicity would increase, lowering the interfacial tension between the water and plastic due to electrostatic repulsion. Hence, the detachment of the ink became easier.

Table 3. Controlled samples without the presence of surfactant at different pH levels

pH	Controlled Sample
11.0	
11.5	
12.0	

Table 4. Deinked PET samples treated with CTAB and SDS at different pH and concentration levels

Surfactant	pH	Concentration of solution		
		25% of CMC	CMC	5xCMC
CTAB	11.0			
	11.5			
	12.0			
SDS	11.0			
	11.5			
	12.0			

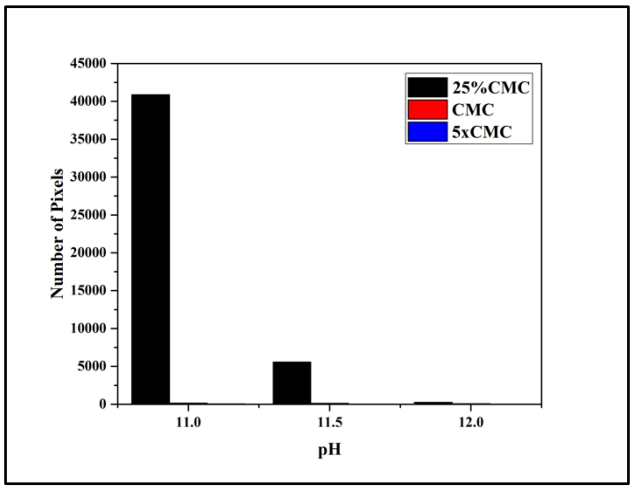

Figure 5. Number of pixels detected on the deinked PET samples with selected CTAB concentrations as a function of pH

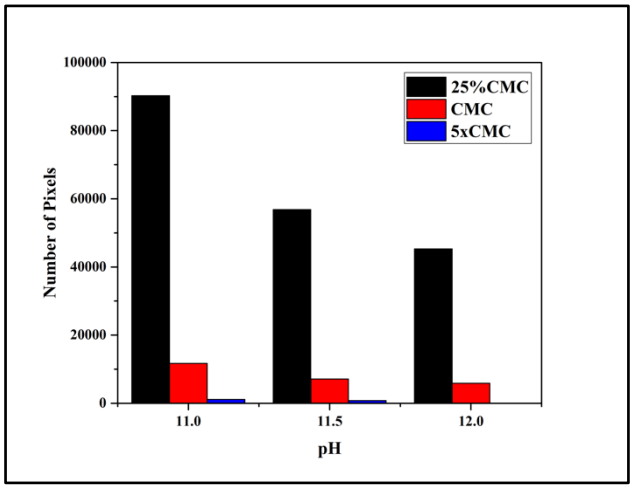

Figure 6. Number of pixels detected on the deinked PET samples with selected SDS concentrations as a function of pH

3.3 Effect of Concentration and Temperature on Deinking of PET Film

The temperature was the next parameter tested with the same goal. Each surfactant was prepared under three levels of CMC, as previously stated: before, during, and after. These solutions were then heated to 30°C, 35°C, and 40°C. The temperature selection was correlated with the early TGA result of the PET ribbon, where the material was found stable at under 122.34°C before it experienced its first weight loss due to evaporation of moisture and some volatile compounds. Moreover, the range of temperature chosen was aligned with the principles of green chemistry as energy used was minimized.

At higher concentrations and temperatures, CTAB showed a superior deinking action compared to SDS. The cationic surfactant recorded a value of 99.98% for ink removal, while the anionic surfactant was 99.29%. As an amphiphilic chemical, CTAB has higher a likelihood of lowering the surface tension between the water and plastic. This droves the surfactant to readily react with the ink thus detaching it effectively.

Table 5. Controlled samples without the presence of surfactant at different temperature

Temperature (°C)	Controlled Sample
30.0	
35.0	
40.0	

Table 6. Deinked PET samples treated with CTAB and SDS at different temperature and concentration levels

Surfactant	Temperature (°C)	Concentration of solution		
		25% of CMC	CMC	5xCMC
CTAB	30.0			
	35.0			
	40.0			
SDS	30.0			
	35.0			
	40.0			

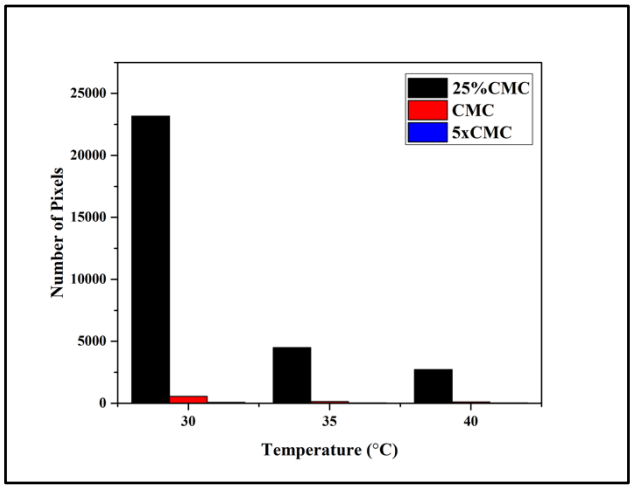

Figure 7. Number of pixels detected on the deinked PET samples with selected CTAB concentrations as a function of temperature

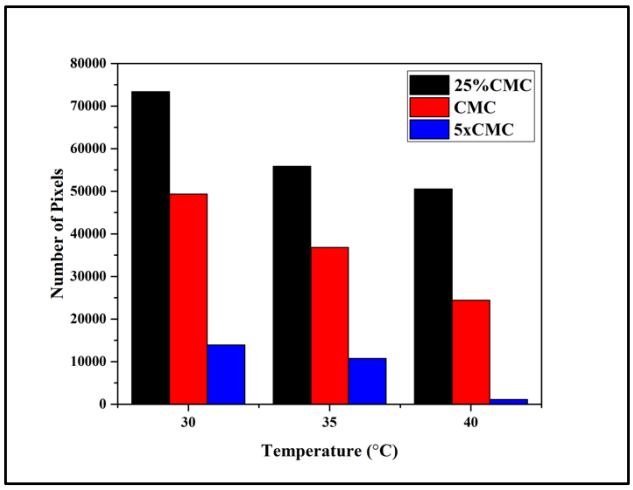

Figure 8. Number of pixels detected on the deinked PET samples with selected SDS concentrations as a function of temperature

4. Conclusion

TGA enabled the detection of the thermal stability and chemical composition of the sample. The presence of volatile substances in the film resulted in the first weight loss of 11.66% at 122.34°C, followed by the second weight loss of 29.52% at 385.51°C due to the rupture of diethylene glycol ($C_4H_{10}O_3$). The cross-linked carbonaceous structures broke down at 654.96°C and 740.30°C, which caused the third (3.77%) and fourth (3.97%) weight loss. A sufficient information on the functional groups that existed within the black ink on the PET's surface has also been gleaned through the characterization of the material by ATR-FTIR. Detachment of several compounds such as intermolecular bonded O-H at 3543.44 cm^{-1} and 3428.31 cm^{-1}, intramolecular bonded O-H at 3055.67 cm^{-1}, N-H at 3317.80 cm^{-1} and 1580.95 cm^{-1}, disubstituted C≡C at 2107.40 cm^{-1}, and C=C at 1611.86 cm^{-1} after the deinking process were noticed as comparison of spectrum were made. The pixel value of the deinked sample from the optical scanning method also supported the findings. For the PET sample immersed in the SDS solution of 5xCMC heated at 40°C and 5xCMC of pH 12, the ink removal percentages were 99.29% and 100.00%, respectively. Meanwhile, in CTAB with a similar environment, the ink removal percentages were 99.98% and 100.00%. All in all, it could be seen that the ink removal rate could give distinguishable results with different types of surfactants paired with such optimum parameters. In this study, CTAB was deduced as an excellent choice for deinking agent over SDS because it lowered the surface tension between the film and water at a much deeper scale, thereby driving effective deinking of PET film.

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