



## Kinetics Study of Acid Hydrolysis of Waste Polyamide-6,6 Using Sodium-1-heptane Sulphonate Surfactant

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### ABSTRACT

In this paper, the depolymerization of waste polyamide-6,6 by using sodium-1-heptane sulphonate as a catalyst was carried out by acid hydrolysis. This method provides the recycling of polyamide into its monomer derivative which is dibenzoyl derivative of hexamethylene diamine. Depolymerization was carried out at different time from 30 min to 180 min by using 0.03 g of sodium-1-heptane sulphonate at 80°C by taking various amount of catalyst. Reaction takes place around 120 min to get 78.23% yield of the product. The product was analyzed by its melting point (154°C) and FTIR spectra and it was found to be same as the pure one. Kinetics shows pseudo first order with reaction rate constant  $6.68 \times 10^{-3}$  minute<sup>-1</sup>.

**Keywords:** Sodium-1-heptane sulphonate, Chemical recycling, Polyamide-6,6, FTIR, DBHMD, Pseudo first order kinetics.

### INTRODUCTION

Today about 400 million tons of plastic products are being made. Due to its outstanding properties, plastics being used in huge quantity in our day-to-day life but only 20 to 30% of plastics is recycled and rest is waste. Polyamide waste are non-biodegradable material and they are very much used nowadays and hence after use gets collected in the environment in one or the other form and creates microplastic pollution, mega plastic pollution<sup>1</sup>. There are many things which are made up of polyamide such as rope, bottles, carpets, etc.<sup>2</sup>. Now a days many methods has been developed for the recycling of polyamide waste such as physical recycling,

mechanical recycling where the polymer waste is washed, cut into small pieces, and then melted and another one is chemical recycling where many other sub processes are carried out to depolymerize polymers such as pyrolysis, solvolysis, partial oxidation, glycolysis, hydrolysis and many more<sup>3-6</sup>. Recycled product obtained by mechanical method are of poor quality while that chemical recycled products are of good quality<sup>7</sup>. In recent past many efforts has been developed for monomerization of polymer waste by many methods<sup>8-9</sup>.

Polyamides is a crystalline polymer which are obtained mainly as nylon-6 and nylon-6,6<sup>10</sup>. Mostly polyamides are obtained



in the form of thermoplastic polymer<sup>11</sup>. Based on the different experiments it is found that for depolymerization, temperature and time required are an important factor which led to the formation of monomer as a product. Nylon-6,6 when depolymerized gets converted to its monomers adipic acid and hexamethylene diamine. Many experiments have been performed by taking different solvents to convert nylon-6,6 into its monomer. At optimum condition the hydrolytic depolymerization of nylon waste in acidic medium gives an efficient result at 80°C<sup>12</sup>.

Surfactants are organic compound which is made up of hydrocarbon chain attached to polar group. Surfactants are of many types depending upon its hydrophilic head as cationic, anionic, nonionic and amphoteric. There are many surfactants which plays an important role in pharmaceutical processes, metal-ligand formation, depolymerization of polymers etc. In one of the experiment cationic surfactants CTMB plays an important role for oxidation of L-glutamic acid by hexacyanoferrate(III) and due to its positive salt effect the reaction rate first increases and then remains constant and shows first order kinetics using Ru(III),  $[\text{Fe}(\text{CN})_6]^{3-}$ <sup>13</sup>. In one experiment sodium lauryl sulphate surfactant is used for determining alpha lipoic acid in some pharmaceutical samples due to presence of 2 sulphur alpha lipoic acid in SLS medium it forms chelate with  $\text{Pd}^{2+}$  hence SLS plays an important role to inhibit the process<sup>14</sup>.

In this work, an attempt was made to depolymerize Nylon-6,6 waste to its derivative form in acidic medium with the help of catalyst which is sodium-1-heptane sulphonate, anionic surfactant in very small amount, plays an important role to give great amount of product dibenzoyl derivative of hexamethylene diamine (DBHMD).

## MATERIALS AND METHODOLOGY

### Chemicals and apparatus

The apparatus consists of 250 mL round bottom flask with water condenser and heating electric furnace. Nylon-6,6 waste was collected, washed, and cut into small pieces. Hydrochloric acid, benzoyl chloride, sodium chloride pallets were of analytical grades.

### Viscosity method for nylon-6,6 and CMC of anionic surfactant

Nylon waste molecular weight was determined by viscosity method using different concentration of nylon-6,6 in m cresol which is used as solvent. For each concentration i.e from 0.0125% to 0.075% flow time was measured and graph was plotted between concentration on x axis and  $[\eta_{sp}]/C$  on Y axis. By using the formula  $[\eta_{sp}]/C = KM^\alpha$ , where  $K$  and  $\alpha$  value for the solvent is  $2.41 \times 10^{-3}$  and 0.6101 intercept and average molecular weight was found.

In this study sodium-1-heptane sulphonate (SHE) is an anionic surfactant which is used as a catalyst. By using drop count method critical miscelle concentration of the surfactant was obtained. 0.1% to 1% concentration of surfactant was prepared by solubilizing surfactant in distilled water. Using stalagmometer number of drops of different concentration was counted and a graph was plotted between concentration (%) verses CMC and from graph CMC of sodium-1-heptane sulphonate was determined.

### Depolymerization of nylon-6,6 at various time interval using sodium-1-heptane sulphonate

Hydrolysis of 3 g of Nylon-6,6 was done using 50 mL of 5N HCl and sodium-1-heptane sulphonate (SHE) of various amount (0.01 g to 0.06 g) in 250 mL round bottom flask and refluxed using water condenser for 2 h at 80°C. The reaction process was carried out at different temperature but it was found that 80°C was an optimum temperature where the rate of reaction is fast, hence after 2 h the reaction mixture was cooled and filtered and neutralized using required volume of 5N sodium hydroxide solution till red litmus turns to blue colour. This neutralised solution is hexamethylene diamine was then treated with benzoyl chloride till the odour of acid chloride gets disappeared. Hexamethylene now gets converted to the product dibenzoyl derivative of hexamethylene diamine (DBHMD) which is recrystallised with ethanol, dried, and weighed. It is found by calculation that by taking 0.03 g of surfactant the highest amount of product is obtained hence further process was carried out by using same procedure by taking 0.03 g of surfactant for depolymerization of 3 g of nylon-6,6 at 80°C but

at various time interval (30 min to 180 min) and found that highest yield of the product DBHMD was obtained by taking 0.03 g surfactant at 80°C by heating the reaction mixture for 120 minute. Melting point of DBHMD was determined and found to be 154°C and through FTIR analysis DBHMD was characterised. Using different parameters kinetic study is obtained.

## RESULT AND DISCUSSION

### Determination weight average molecular mass and CMC by surface tension method

Weight average molecular mass of Nylon-6,6 by using Ostwald's viscometer was determined by plotting a graph between  $[\eta_{sp}]/C$  (x axis) and concentration (%) (y axis) is 27500, by using formula  $[\eta_{sp}]/C = KM^\alpha$  where  $K$  and  $\alpha$  value of the solvent are  $2.41 \times 10^{-3}$  and 0.6101, respectively and intercept obtained by plotting intrinsic viscosity vs concentration is 1.2230.

0.1% to 1% of concentration of sodium-1-heptane sulphonate was prepared in distilled water. Number of drops were recorded using stalagmometer and surface tension of various concentrations was calculated by the formula,

$$\gamma_{sol} = \rho_{sol} \times \eta_{H_2O} \times \eta_{sol} \times \gamma_{H_2O}$$

Where,  $\gamma_{sol}$  Surface tension,  $\rho_{sol}$  and  $\rho_{H_2O}$  are density of solution and density of water,  $\eta_{H_2O}$  and  $\eta_{sol}$  are no. of drops of water and solution respectively. CMC obtained by plotting a graph between concentration (x axis) and surface tension (y axis) was 0.302 mol/dm<sup>3</sup>. It was found that there is no effect of CMC on reaction process.

### Escalation parameter for depolymerization of nylon-6,6 at different time interval using different amount of sodium-1-heptane sulphonate

Reaction mixture containing 3 g nylon-6,6, 50 mL 5N HCl and sodium-1-heptane sulphonate (0.01 g to 0.1 g) in 250 mL round bottom flask attached with thermometer and stirrer was depolymerised at 80°C using water condenser for 2 h and result obtained shows that highest yield obtained by taking 0.03 g of surfactant shown in Figure 1.

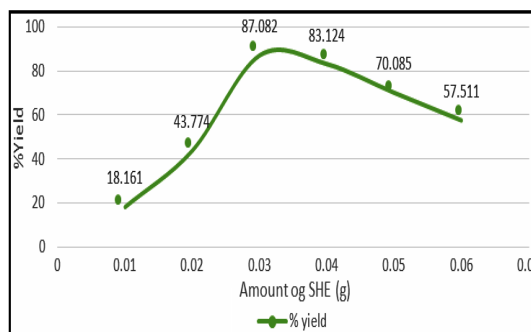


Fig. 1. Percentage yield of various amount of sodium-1-heptane sulphonate

From Fig. 1 it is seen that by taking 0.03 g of sodium-1-heptane sulphonate was taken as catalyst and the same amount of reaction mixture was refluxed at 80°C for different time interval (30 min to 210 min) and hence the result obtained showing highest %yield of product in 120 min shown in Fig. 2. Due to very less concentration of surfactant, pH does not change during whole reaction process. In many experiments we have seen that in absence of surfactant<sup>12</sup> the rate of reaction is very slow and got less amount of product but due to addition of even small quantity of surfactant the rate of reaction is fast and product obtained is high.

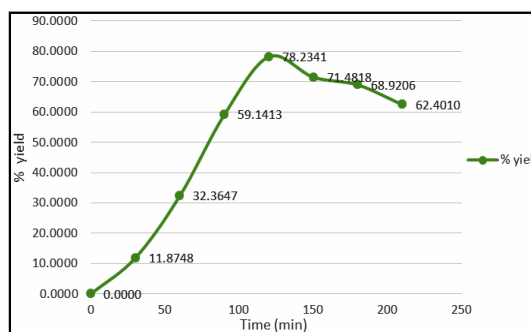


Fig. 2. Percentage yield of DBHMD at various time interval

### Kinetics of nylon-6,6 waste depolymerisation

Based on benzoyl derivative of hexamethylene diamine the kinetic study was carried out at escalate parameter. The amount of reacted and unreacted nylon-6,6 was obtained by the amount of dibenzoyl derivative of hexamethylene diamine. From the kinetic study we get to know that it shows pseudo first order reaction, expressed by the equation given below.<sup>15</sup>

$$-\frac{d[\text{Nylon-6,6}]}{dt} = k[\text{Nylon-6,6}] [\text{HCl}]^m [\text{H}_2\text{O}]^n [\text{SHE}]^p \quad (1)$$

Due to excess amount of HCl and H<sub>2</sub>O it

gets negligible and very small amount of SHE is used as catalyst and hence concentration of SHE also gets negligible hence the above reaction can now be expressed as;

$$-\frac{d[\text{Nylon-6,6}]}{dt} = k'[\text{Nylon-6,6}] \quad (2)$$

If we take the initial amount and some amount after some time interval as  $[\text{Nylon-6,6}]_a$  and  $[\text{Nylon-6,6}]_b$ , then the integral of equation 2 can be written as

$$\ln\left[\frac{[\text{Nylon-6,6}]_a}{[\text{Nylon-6,6}]_b}\right] = k't \quad (3)$$

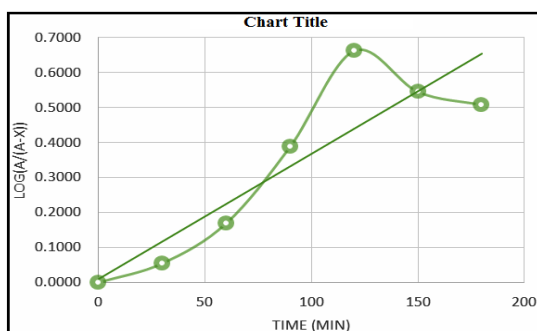
The above equation can be expressed as  $\ln\left[\frac{a}{a-x}\right]$  where  $a$  is initial weight and  $(a-x)$  is weight after some time and finally above equation can be written as;

$$\ln\frac{a}{a-x} = k't \quad (4)$$

The optimum conditions set earlier and the order of reaction was determined by doing depolymerization of nylon-6,6 using catalyst. From Table 1 the amount of product was obtained at different time intervals and data tabulated in Table 1 shows that it is pseudo first order kinetics because hydrochloric acid is taken in excess amount and catalyst used is negligible, since the rate equation for first order reaction<sup>15-16</sup> is given as  $K=(2.303/t) \log(a/(a-x))$ , if this equation is rearranged then we get,  $\log(a/(a-x)) = Kt/2.303$ . By plotting graph between time (min) on x axis and  $\log(a/(a-x))$  on y axis we get a straight line passes almost through origin and slope gives rate constant value  $6.68 \times 10^{-3} \text{ min}^{-1}$  shown in Figure 3.

**Table 1: Depolymerization of nylon-6,6 waste using SHE as catalyst**

Time (min)	Amount of nylon-6,6 waste (gram)	Amount of SHE (gram)	Amount of DBHMD (gram)	Amount of nylon-6,6 reacted (gram)	Amount of nylon-6,6 unreacted (gram)	$\log(a-x)$	$a/(a-x)$	$\log(a/a-x)$
0	3.00	0.03	0.00	0.00	0.00	0.47	1.00	0.00
30	3.00	0.03	0.51	0.36	2.64	0.42	0.13	0.54
60	3.00	0.03	1.40	0.97	2.03	0.30	1.48	0.17
90	3.00	0.03	2.50	1.77	1.23	0.08	2.45	0.38
120	3.00	0.03	3.40	2.35	0.65	-0.18	4.50	0.66
150	3.00	0.03	3.06	2.14	0.86	-0.06	3.50	0.54
180	3.00	0.03	2.95	2.07	2.95	-0.03	3.22	0.50



**Fig. 3. Graphical presentation**

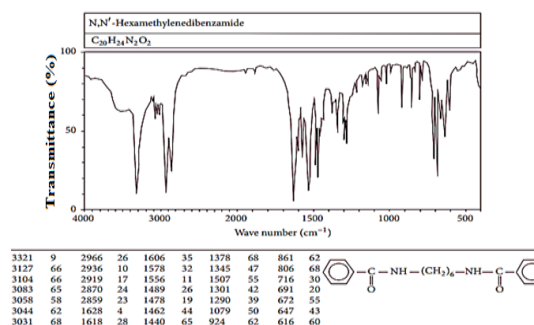
### FTIR spectra analysis

The FT-IR spectral data<sup>17</sup> of the product obtained DBHMD and the controlled DBHMD was recorded and found that various peaks obtained which was found that most of the peaks of product DBHMD were same as that found in controlled DBHMD shown in Fig. 4 and 5 and Table 2. From Fig. 5 we see that there is presence of hydrogen bond shown by sharp bands. Bands obtained at  $3017 \text{ cm}^{-1}$ ,  $1423 \text{ cm}^{-1}$ ,  $1629 \text{ cm}^{-1}$ ,  $3309 \text{ cm}^{-1}$  indicate

the presence of C-H, C-C, C=O, N-H. There are many bands between  $1600$  to  $400 \text{ cm}^{-1}$  which indicate presence of stretching bands.

**Table 2: FTIR spectra values of DBHMD**

Compound	Wavelength ( $\text{cm}^{-1}$ )
C-H	3071
C-C	1423
C=O	1629
N-H	3309



**Fig. 4. FTIR Spectra of controlled DBHMD<sup>12</sup>**

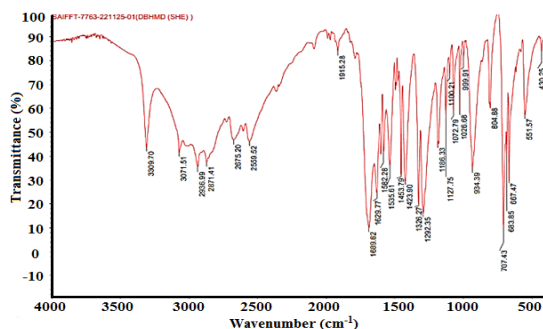


Fig. 5. FTIR spectra of product DBHMD

### CONCLUSION

Result reveals that anionic surfactant sodium-1-heptane sulphonate (0.03 g) which is used as catalyst helps to degrade nylon-6,6 waste at 80°C of 120 min heating and gives better result. it was

found that there is no relation between CMC and the amount of sodium-1-heptane used in the reaction. Melting point and FTIR spectra reveals that product obtained is dibenzoyl derivative of hexamethylene diamine. It shows pseudo first order kinetics and rate of reaction is  $6.68 \times 10^{-3}$  minute<sup>-1</sup>. In future, other than anionic surfactant other type of surfactant can be used for depolymerization and get different results.

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### Conflict of Interest

The authors declare no conflict of interest.

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