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**Publications**

Kinetics Study of Acid Hydrolysis of Waste Nylon-6,6 using Anionic Surfactant

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Abstract

The depolymerization reaction of nylon-6,6 is carried out by acidic hydrolysis in the presence of various amounts of sodium dodecyl benzene sulfonic acid (SDBS) (0.02 to 0.07 g) surfactant used as a catalyst at 80 °C and at a different time interval (120 to 240 min). The maximum yield was obtained when 0.05 g SDBS was added to the reaction mixture as a catalyst and 180 min. The reaction mixture was neutralized by 5N NaOH, and the hexamethylene diamine obtained was converted into the Dibenzoyl derivative of hexamethylene diamine (DBHMD), which was filtered, dried, and weighed. The yield was found to be 87.14 %. The characterization was done by the melting point determination and FTIR spectra. The information obtained was in accordance with the literature value. This reaction has followed first-order kinetics with a rate constant of reaction 8.31×10-3 min -1. The IR recorded clearly reveals that the product obtained is pure.

*Keywords*: Nylon-6,6; SDBS; DBHMD; Depolymerization; Kinetics.

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1. Introduction

Plastic is a fabricated material that can be produced in any form. Various plastics have been used in distinct situations, and at present, their uses are increasing hence are a major source of solid waste pollution. Solid waste such as polyethylene, polyamide, and various other poly-waste materials are either dumped or burned after use which is economically dangerous for human life**.** Polymers have been regarded as a powerful coating material owing to their excellent barrier qualities, used in aeronautical equipment, etc. [1,2]. Recycling plastics has become much more important, but technology has not been developed so far. Only a limited amount of poly-waste has been recycled by material, thermal, or chemical recycling to get the desired amount of useful product [3,4]. Among the polyamide nylon is plastic which is widely used. Its depolymerization was explored over 30 years [5]. Polymer waste recycling using an ionic solvent to get the monomer is used due to the unique properties of ionic liquids [6].

The consumption of nylon waste is much less than polyethylene, polyester, and many more plastic wastes. The melting point of nylon is high and has less solubility hence used in a wide range of application. The chemical recycling of nylon is usually elicited by pyrolysis, hydrolysis, or aminolysis [7]. Iwaya and co-workers reported that nylon 6 could be recycled by hydrothermal process into Ɛ-caprolactam and Ɛ-aminocaproic acid.]. Amit Kumar and co-workers studied the depolymerization of nylon in the presence of a ruthenium catalyst and found that the monomer obtained can be reused by converting it into its original polymer form [8]. Chen and his co-worker investigated the depolymerization of nylon-6 using a heteropolyacid catalyst and produced its monomer, i.e., Ɛ-caprolactam[9]. Nemade and Zope investigated the chemical degradation of nylon waste using different solvent among which formic acid is found to be the best solvent which dissolves polyamide waste and produces its monomer [1]. Many scientists have performed work on the chemical recycling of polyamide waste through different methods [10-12]**.** Chanda showed various chemical aspects of polymer recycling through conventional and unconventional methods, such as enzymatic degradation, microwave irradiation, superfluids, and many more[13]. Using various concentrations of hydrogen peroxide, Prasetyaningrum *et al*. depolymerized K-Carrageenan and determined its kinetic study by oxidation reaction (14). Patil and Madhamshettiwar reported that nylon-6,6 is depolymerized by hydrolysis reaction using HCl, and the product obtained is a dibenzoyl derivative of hexamethylene diamine [7].

Significantly less work has been developed for the depolymerization of nylon-6,6 polymer. In the present work, depolymerization of nylon-6,6 waste by acid hydrolysis using sodium dodecyl benzene sulphonic acid as a catalyst has been investigated. The kinetics of hydrolysis is studied by changing the concentration of SDBS catalyst and time at 80 °C temperature. Based on data on kinetics, the rate of reaction and order of reaction were determined.

**2. Experimental**

**2.1. *Chemicals and reagents***

All chemicals used in the depolymerization of nylon waste were of analytical grades, such as sodium hydroxide, hydrochloric acid, benzoyl chloride, sodium dodecyl sulphonic benzene acid, and m cresol, supplied by E Merck. Nylon waste was collected. Nylon waste was first frozen to escalate brittleness and then crushed into pieces.

**2.2. *Determination of viscosity average molecular weight***

By using Ostwald’s viscometer, the viscosity average molecular weight of nylon-6,6 waste powder was determined. M- cresol is used as a solvent, and by dissolving various concentrations (0.0125 to 0.075 %) of nylon-6,6, waste was prepared, and flow time was recorded. From the graph, the intercept of concentration Vs. [𝜂𝑠𝑝]/𝐶 obtained is 1.2248. The molecular weight was calculated by using the formula [𝜂𝑠𝑝]/𝐶 = 𝐾𝑀𝛼 where 𝐾 and 𝛼 values for the solvent are 2.4 × 10−3 and 0.61 at 28 °C (room temperature), respectively.The average molecular weight of nylon waste obtained was 27480.

**2.3. *Determination of CMC of surfactant***

Sodium dodecyl benzene sulphonic acid (SDBS) is used as a catalyst in this study. It is an anionic surfactant. The critical micelle concentration (CMC) of SDBS is determined by the surface tension method. Various concentrations of SDBS (0.1 to 0.7 %) in water are prepared. Using a stalagmometer, a number of drops were recorded, a graph was plotted between concentration (X-axis) versus surface tension (Y-axis**),** and CMC was calculated.

**2.4. *Depolymerization of nylon waste using various amounts of SDBS at different time intervals***

Gravimetrically the optimum parameters for depolymerization of nylon-6,6 waste were determined. 3 g of Nylon-6,6 waste powder was added to 50 mL of 5 N HCl and various amounts of SDBS (0.02 to 0.07 g) as catalyst was added and refluxed at 80 °C for 2 h in 250 mL round bottom (RB) flask equipped with a reflux water condenser, stirrer, and thermometer. After 2 h refluxing RB reaction mixture was cooled and filtered. The filtrate was then neutralized with the required volume of 5 N NaOH till red litmus changed to blue and then treated with benzoyl chloride with vigorous shaking until the odor of acid chloride disappeared. HMD, the solution gets converted into DBHMD as a product, weighed, and recrystallized with ethanol. Various amounts of products are obtained by various amounts of SDBS. The highest amount of product was obtained by 0.05 g of SDBS; hence this value was taken for further kinetic study at different time intervals (2 to 4 ½ h). The melting point of dried DBHMD powder was found to be 157 °C. FTIR spectra also characterized the DBHMD, and it was compared to the spectra of standard DBHMD. By using optimal parameters, a further kinetic study was determined. The main intention of the work is to determine the kinetics; hence the temperature stability and its measurement are important.

**3. Results and Discussion**

**3.1. *Determination of average molecular weight of Nylon-6,6 waste powder by viscosity method***

By plotting a graph [𝜂𝑠𝑝]/C on the Y-axis versus concentration on the Y-axis, the viscosity average molecular weight of nylon-6,6 was determined. The intercept (𝜂i) at ordinate was 1.2248. Using the formula [𝜂𝑠𝑝]/𝐶 = 𝐾𝑀𝛼, the average molecular weight was calculated where 𝐾 and 𝛼 value of the solvent is 2.4 × 10−3 and 0.61, respectively. The average molecular weight of nylon-6,6 waste powder was 27481.

**3.2. *Determination of CMC by drop count method***

Various concentrations of SDBS (0.1 to 0.7 %) were prepared in distilled water. By using a stalagmometer, a number of drops were recorded for each concentration. Surface tension (γsol) was calculated by using the formula,

Where ρsol and ρH20 are densities and water, ηH2O and ηsol are no. of drops of water and solution, respectively. The graph plotted between concentration on the X-axis and surface tension on the Y-axis and CMC of SDBS was 0.02869 M.

**3.3. *Optimization parameter for depolymerization of Nylon6,6 waste using various amounts of SDBS at different time intervals***

The depolymerization of nylon-6,6 waste was studied by acid hydrolysis using nylon-6,6 waste powder, various amounts of SDBS (0.02 to 0.07 g), and 50 mL HCl (5 N), and was refluxed using a water condenser at 80 °C for 2 h. Results show an increase in depolymerization of nylon-6,6 till 0.05 g of SDBS, and then a sudden decrease in depolymerization was observed. About 61.27 % yield was obtained by adding 0.05 g of SDBS with other reactants for 2 h at 80 °C. Thus 0.05 g SDBS is an optimum amount that gives the highest amount of product (Table 1).

Table 1. A minimum amount of SDBS is used for the depolymerization of Nylon-6,6 waste.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sl. No. | Amount of nylon waste (g) | Amount of SDBS (g) | Amount of DBHMD (g) | Amount of reacted nylon (g) | Amount of unreacted nylon (g) | % Yield |
| 1 | 3 | 0.02 | 2.2481 | 1.5703 | 1.4296 | 52.34 |
| 2 | 3 | 0.03 | 2.4196 | 1.6901 | 1.3098 | 56.33 |
| 3 | 3 | 0.04 | 2.5417 | 1.7754 | 1.2245 | 59.18 |
| 4 | 3 | 0.05 | 2.6318 | 1.9451 | 1.0548 | 61.27 |
| 5 | 3 | 0.06 | 2.5866 | 1.8761 | 1.1238 | 60.22 |
| 6 | 3 | 0.07 | 2.3582 | 1.8215 | 1.1784 | 54.90 |

Concentration of HCl= 5N, 50 mL, Temperature =80 °C, Time= 2 h.

Depolymerization was carried out by taking 3 g nylon-6,6, 5 0 mL HCl (5 N), and 0.05 g SDBS and temperature at 80 °C by varying the refluxing time 2 to 5 h. It was found that the percentage yield of the product increased from 61.12 to 87.50 % and then gradually decreased to 74.18 %. This indicates that 3 h is an optimum reflux time (Table 2).

Table 2. Kinetic order of depolymerization of Nylon -6,6 Waste.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sl. No. | Heating time (min) | Amount of Nylon-6,6 | Amount of DBHMD (a) (g) | Reacted nylon waste (x) (m) | Unreacted nylon waste [A] (m) | % Yield |
| 1 | 0 | 3 | 0 | 0 | 3 | 0 |
| 2 | 120 | 3 | 2.6318 | 1.8383 | 1.1616 | 61.27 |
| 3 | 150 | 3 | 2.3512 | 2.3512 | 0.6487 | 78.37 |
| 4 | 180 | 3 | 3.7582 | 2.43 | 0.3748 | 87.50 |
| 5 | 210 | 3 | 3.4854 | 2.4346 | 0.5653 | 81.15 |

Concentration of HCl = 5 N, 50 mL. Temperature = 80 °C

**3.4*. Kinetic study of depolymerization of Nylon-6,6 waste powder***

The kinetic study was carried out on the basis of the benzoyl derivative of the product at optimum parameters. The weight of reacted and unreacted nylon-6,6 was determined from the weight of the product DBHMD obtained. From the kinetics equation of nylon-6,6 depolymerization, it is noted that it is a pseudo-first-order reaction hence equation can be expressed as follows:

(1)

The more amount of H2O and HCl and a small amount of SDBS as a catalyst, the equation can be written as follows,

(2)

If the initial amount of nylon-6,6 is expressed as [nylon-6,6]0 and the amount at some time interval is expressed as [nylon-6, 6], then the integral of (Eq. 2) can be written as,

(3)

Nylon-6,6 is in a solid state; thus, its amount can be expressed in terms of weight. Therefore, Eq.3 can be written as:

(4)

Where a and (a-x) are initial weight and weight at some time interval, respectively **(**15**)**. Fig. 1 shows the relation between log (a/(a-x)) and reaction time. The slope of the plot gives the reaction rate constant of hydrolysis.

Table 3. Order of depolymerization of Nylon-6,6 waste.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Time (min) | a-x | Log (a-x) | (a/a-x) | log (a/a-x) |
| 0 | 3 | 0.4771 | 1 | 0 |
| 120 | 1.0548 | 0.0231 | 2.8440 | 0.4539 |
| 150 | 1.0706 | 0.0296 | 2.8021 | 0.4474 |
| 180 | 0.3857 | -0.4137 | 7.7776 | 0.8908 |
| 210 | 0.7657 | -0.1159 | 3.9178 | 0.5930 |

When the graph was plotted between log (𝑎 − 𝑥) and time (min), a straight line of the negative slope was obtained, which proves that it is a first-order reaction in nature (Table 3 and Fig. 1). Hence the rate equation for the first-order reaction is,

𝐾 = (2.303/𝑡) log (𝑎 / (𝑎 − 𝑥)); if this equation is rearranged as

(5)

It is an equation of type,

Fig. 1. Graphical representation between time (min) and log (a-x).

Fig. 2. Graphical representation between time (min) and log(a/(a-x)).

The above equation can also be rearranged as log (𝑎 / (𝑎 − 𝑥)) = 𝐾𝑡/2.303; this equation is a type of 𝑦 = 𝑚𝑥. Therefore, when the graph is plotted between log (𝑎 / (𝑎 − 𝑥)) and time in a minute, a straight line is obtained, which passes through the origin. Hence, we can say that it is the first-order nature of depolymerization of nylon waste reaction [15](Table 3, Fig. 2). A straight line that passes through the origin gives the value of reaction rate constant 8.3×10-3min -1.

A large amount of hydrochloric acid was used, and its concentration does not affect any important value; hence the reaction is a pseudo-first-order reaction. From the above result, we can say that depolymerization of nylon-6,6 waste is a first-order reaction with respect to nylon-6,6 concentration, as the concentration of HCl is high and the concentration of SDBS is negligible, and it acts as a catalyst; hence it does not change appreciably during the course of the reaction.

**3.5. *Characterization of DBHMD by FTIR spectroscopy***

With the help of FTIR spectra, the IR spectra of controlled DBHMD and the DBHMD obtained by the acid hydrolysis of nylon-6,6 waste powder was found to be identical with various peak, which can be compared through Figs. 3 and 4.

All bands that appeared are sharp, which shows that there is hydrogen bonding. The band obtained at 2835 cm-1 indicates the presence of C-H stretching, 3310.57 cm-1 indicates the presence of N-H stretching, 1423.99 cm-1 indicates the presence of C-C stretching, and 1686.21 cm-1 indicates the presence of C=O stretching. The sharp band at the left hand of spectrum 3310.57 cm-1 in this spectrum shows N-H stretch amide functional group because it shows the combined feature of amine and ketone as it has both the N-H bond and the C=O bond [16].Many peaks obtained between 1500-400 cm-1 represent different types of vibrations that occur in the molecule, including different stretching. FTIR spectrum obtained for the product obtained was found to be similar to that of the controlled product; hence similar explanation is applicable.

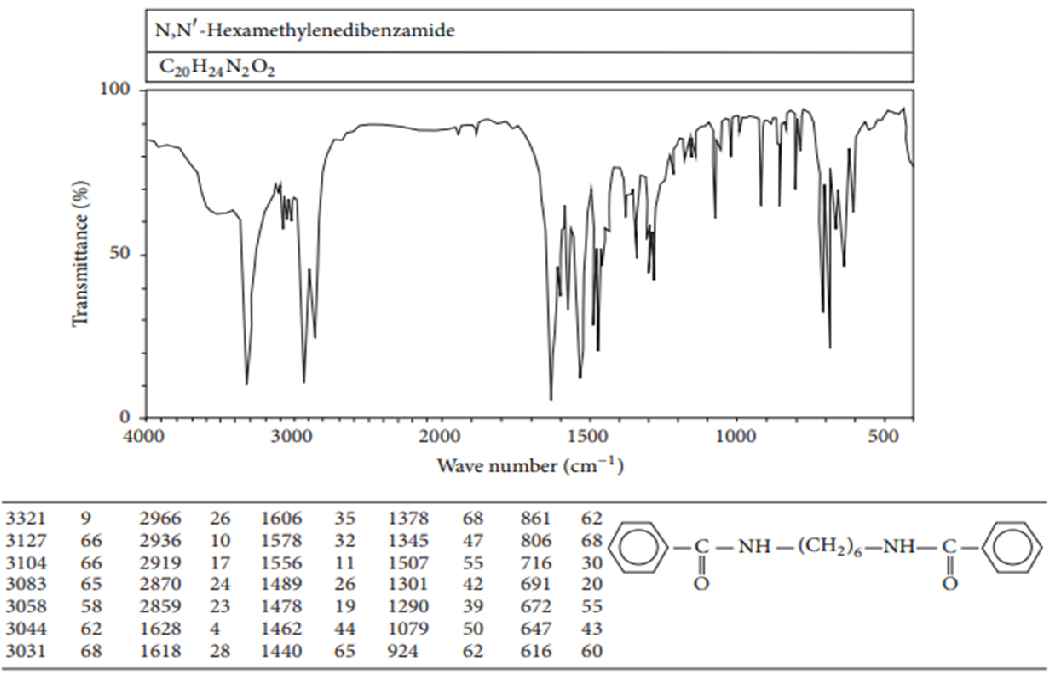


Fig. 3. FT-IR Spectra of DBHMD (controlled) [7].



Fig. 4*.* FT-IR spectra of DBHMD (product).

**4. Conclusion**

In conclusion, we report here the kinetics of hydrolysis of nylon-6,6 using sodium dodecyl benzene sulphonic acid surfactant as a catalyst. At first, we found out the average molecular weight of nylon-6,6 polymer waste by viscosity method. Sodium dodecyl benzene sulfonic acid is an anionic surfactant used as a catalyst; hence, the drop count method determined its critical micelle concentration. It was found that there is no relation between CMC and the amount of SDBS used for the depolymerization of nylon waste.

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