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COMPARATIVE STUDIES ON CHEMICAL RECYCLING (DEPOLYMERIZATION) OF POLYURETHANE SCRAP MATERIAL

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ABSTRACT

Wide range of properties with respects to comfort, safety, designs and particularly in weight reduction, made the polyurethane (PU) foam, one of the most versatile material as a replacement to rubber. Superior material properties of PU finds wider range of application, in the industrial sectors such as carpets, automobile cushioning, refrigeration and insulations. This results in the generation of bulk of waste including pre and post consumer waste, which affects environment in many aspects of pollution. Present awareness of ecological aspects by public and also by politicians, researchers have been attracted to carry out the effective recycling of PU waste. Many techniques have been involved to carry out the recycling of PU scrap including physical (mechanical) recycling as well as chemical recycling. Amongst them, the route of chemical recycling is preferable, because of its ability to yield recycled products that can be used as an alternative to virgin raw material. In this communication, "Depolymerization" of PU scrap with varying solvent mixtures (Polyol + Catalyst) at different temperatures is reported. Depolymerization solvents were developed for glycolysis of PU foam. Measurement of hydroxyl value was found to be excellent to study the extent of depolymerization. PU foam used to study the depolymerization was found to have the molecular weight in the order of 10^6. The dissolution time at 150°C in solvents polyethylene glycol (PEG) and diethylene glycol (DEG) were found to be 50 minutes, and 15 minutes, respectively, while it was 3 minutes for both solvents at 200°C. Energy of activation was found to be 52.82 KJ $mole^{-1}$ and 66.78 KJ $mole^{-1}$, respectively for DEG and PEG. Similarly, the rate constants calculated were found to be 1.18×10^{-4} $mole^{-1}$ and 3.39×10^{-5} $mole^{-1}$, respectively for DEG and PEG, which clearly indicates that glycolysis of PU foam proceeds at a faster rate in DEG.

Key words: Depolymerization, Solvents, Polyurethane, Polyol, Chemical recycling.

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INTRODUCTION

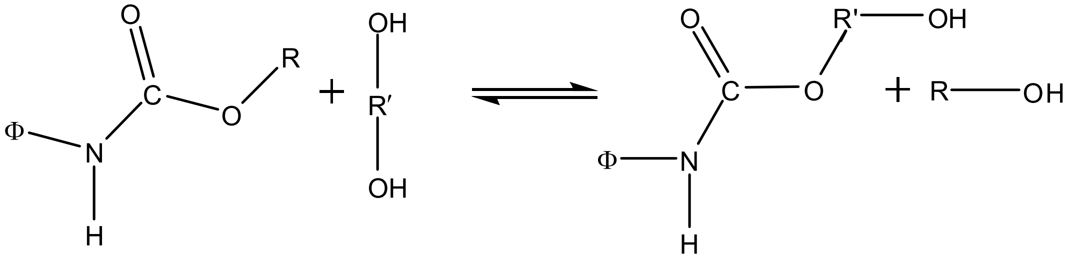
PU foam is an innovation by Otto Bayer in 1937. Now a days, it is found to be the best substitute to the rubber because of its versatile properties. Polyurethane consists of polymers derived from the reaction between isocyanate and polyols[1]. Owing to its excellent physical properties in respect to good flexibility, variety of designs, ability to get molded and weight reduction, it finds extensive applications in the fields of automobile cushioning, interiors, carpet, refrigeration, insulations and as laminates for construction panels[2]. As the cleavage of polyurethane with water proceeds very slowly, it is not surprising since many applications for this class of polymers rely on their resistance to water at elevated temperature. Unfortunately as like the other man made synthetics, the darker side of this glowing industry is the saturation of several hundred tons of polyurethane waste daily across the world. This mainly includes post consumer wastes such as used in car cushioning, outdated panels and foams of refrigerator. Similarly, a huge volume is accumulated during the productions steps. (e.g. trimmings, edging, molding, cutting of specific shapes). About 15-20% by weight of total polyurethane foam production is disposed as a scrap during block production, which requires subsequent cutting. Since polyurethanes are generally classified as thermosetting polymers they cannot be melted and reprocessed by extrusion process, without suffering extensive degradation. Hence, polyurethane has to be recycled effectively[3].

In USA and Europe, most of polyurethane scrap is still disposed of in landfills after compacting it into brickets with a density of approximately 500 kg/m^3, which affects adversely the ecology of surroundings because when polyurethanes get buried down the soil, it get broken down by the action of water to give urea. Similarly, the options of burning polyurethane scrap could not be accepted, it may sends oxides of nitrogen, hydrocyanic acid, carbon dioxide and others toxic materials into the atmosphere[4]. Many scientists have dedicated their research in finding the most sustainable route of recycling of polyurethane foam that mainly include physical as well as chemical methods. The physical recycling of polyurethane is mainly working on the principle of rebond and regrind technologies, but the resultant recycler leads to adverse change in mechanical properties of new products. To overcome this problem, the companies like Hennecke is working on comparatively new techniques as; REBOTEC™ (Modern Rebond Technology) and REMOTEC™ (Rebond Molding Technology)[5-6]. The REBOTEC™ developed a semi automatic as well as fully automatic flake-binder mixing process, for the manufacture of top quality blocks of PU. Where as REMOTEC™ enables the molding of rather complex polyurethane shape, which are produced from rebonded materials in a fully automatic process. Although it seems to be lucrative process of scrap recycling, but there are some drawbacks due to which now a days, more intension has been paid towards chemical recycling, these are :

- The second generation product made with physical recycling methods is inferior regarding the mechanical stress and strain.
- Due to particle size of grinded polyurethane powder, a superior appearance of surface is not easily achievable.
- Cost for collection and separation of scrap from contaminants as fabric, fiber, metal strips, wire inserts is relatively high.

The method of chemical recycling; depolymerization has the ability to produce the recycled product that can be used as an alternative to virgin starting polyol. True example of this process has been proposed by ICI plc[7]. The top quality product designed to be glycolysed and new raw material generated will be used in the manufacture of fresh flexible polyurethane foam. Besides glycolysis, there are various possible chemical processes such as hydrolysis, alcoholysis, aminolysis and pyrolysis. The name for each depolymerization reactions depends on reagent used to affect it[8].

Among all available techniques, we have adapted a route of glycolysis, which has ability to yield a monophasic product as a trans-esterification reaction involving a breaking of urethane bond, which get increased due to pyrolysis reaction at the glycolysis temperature. Glycolysis is nothing but a thermo-chemical interaction between polyurethane and hydroxyl containing polyol. Glycolysis products could be used as an industrial adhesive in some cases[9]. Recently in the experiment performed by Nikje et al.[4], glycolysis using glycerol as a solvent already proved its effectiveness in the successful recovery of polyol. Bauer from Technology Institute, Aalen has demonstrated successful recovery of polyol from car seats and attached polyester and nylon fabrics[10]. Simioni from the University of Padua has recovered polyols from the microcellular elastomers such as shoe sole scrap[11]. The chemistry of glycolysis involves the break down of urethane bond, in which polymer chain is depolymerized to a mixture of liquid oligomers, which proceeds according to the following reaction;



Where; Φ = urethane linkage

Hereby, we report on the depolymerization of polyurethane foam scrap by treatment with diethylene glycol and polyethylene glycol with alkaline metal hydroxide (sodium hydroxide) as a catalyst at various reaction conditions. The resultant solution (Dissolved PU + Polyol + catalyst) was characterized by means of classical methods. Various relationships regarding hydroxyl number[12] of solutions and reactions conditions were reported.

EXPERIMENTAL

Materials

The scrap of polyurethane foam waste was obtained from refrigerator dismantling station. Diethylene glycol was a colourless viscous liquid having a specific gravity of 1.116 g/cm³, molecular weight 106.12, and refractive index 1.446 – 1.447. The polyethylene glycol was a colourless liquid having viscosity of 85-105 centi poise at 20°C, specific gravity of 1.126 g/cm³ at 20°C and molecular weight approximately 380-420, was purchased from Loba Chemicals Ltd. (India) The sodium hydroxide used was in the form of white flakes purchased from S.D. fine chemicals Ltd. (India)

Molecular weight determination of PU foam

The viscosity average molecular weight of PU foam was determined using Ostwald viscometer. The flow time of solutions of various concentrations prepared in solvent di-methyl formamide was recorded. The intrinsic viscosity (Intercept = 6.084) of the graph η_{sp}/C against concentrations was used to calculate the molecular weight of PU using the formula $[\eta_{sp}/C] = k.M^{\alpha}$, where the values of the constants k and α for above solvents are 0.71 and 3.64×10^{-4}, respectively. (Fig. 1). The molecular weight of PU foam was found to be 0.88×10^{6}.

Depolymerization by glycolysis of PU at room temperature and varying quantities of sodium hydroxide

In five different 50 mL capacity beakers, 30 g DEG was added. Each beaker was charged with 1 g of PU foam. The quantity of sodium hydroxide was varied from 1 g to 5 g. The beakers were partially closed with lid and stirred frequently. The hydroxyl values of each sample were recorded after the reaction time of 13 days.

Depolymerization by glycolysis of PU at various temperatures

The glycolysis of PU foam was carried out at temperatures 50, 100, 150 and 200°C using optimized amount of sodium hydroxide (6 g). The solvents used for glycolysis in these experiments were PEG and DEG each of 30 g. Polyol and sodium hydroxide were taken in three-necked round bottom flask, provided with reflux condenser and thermometer. It was heated gradually in oil bath to get homogeneous mixture and then the pieces of PU foam having dimension of 1 cm × 1 cm were charged in the flask. The reactions were carried out at different time interval such as 30, 60, 90, 120 and 150 minutes.

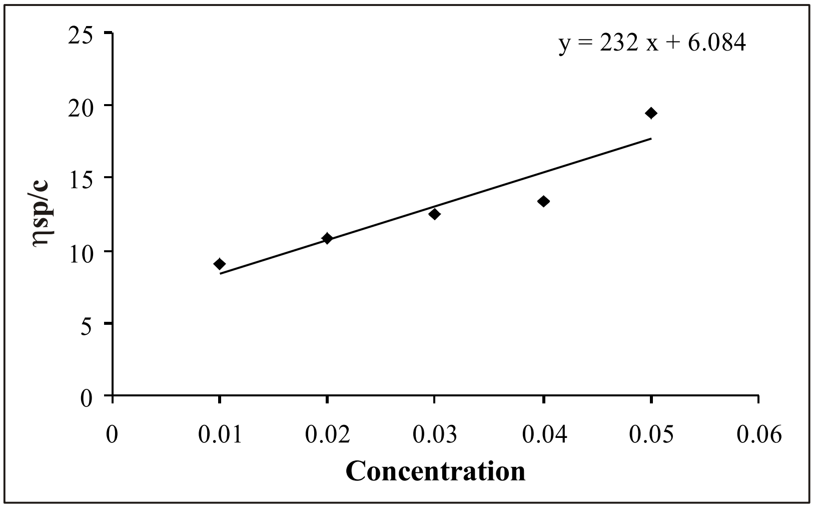


Fig. 1: Variation of intrinsic viscosity with concentration

Dissolution of PU in DEG, PEG and ethylene glycol (EG)

Very simple method was adapted to study the dissolution time of PU foam in different solvents such as PEG of molecular weight 200 and 400, DEG of molecular weight 106 and EG of molecular weight 62 .The time from immersing the PU foam to its complete disappearance was recorded and is listed in Table 1.

Table 1: Dissolution time of PU foam in various glycol solutions using 6 g sodium hydroxide

Glycol	Molecular weight	Temp. (^{o}C)	Dissolution time (min)
DEG	106	150	15
PEG	200	150	28
PEG	400	150	50
EG	062	180	09
DEG	106	200	03
PEG	400	200	03

Determination of hydroxyl value

The reaction mixtures were withdrawn at a definite desired time interval, which contain polyol and other oligomers. polyol have terminated hydroxyl group. The hydroxyl values of each solvent were determined by the formula

$$\text{Hydroxyl value} = \frac{(B - S) \times N \times 56.1}{W} \qquad ...(1)$$

Where; N = Exact normality of KOH,

W = Weight of sample in g,

B = Blank reading and

S = Sample reading

RESULTS AND DISCUSSION

PU foam depolymerized with its dissolution in various solvents. Depolymerization of PU foam was very much difficult without using catalyst, even if the cubes of PU foam were kept immersed for several days at room temperature and at elevated temperature of 50°C, it was recorded that there was no change in the size of cubes. However, the size of the cubes was found to decrease slightly in the presence of catalyst sodium hydroxide at the same conditions of temperature and time (Fig. 2). It was also observed that the sharp edges of the cubes disappeared. PU foam depolymerized by glycolysis using the solvents PEG and DEG, as a result of this, there was formation of hydroxyl group terminated polyol and oligomers. The extent of depolymerization was studied by recording the hydroxyl values.

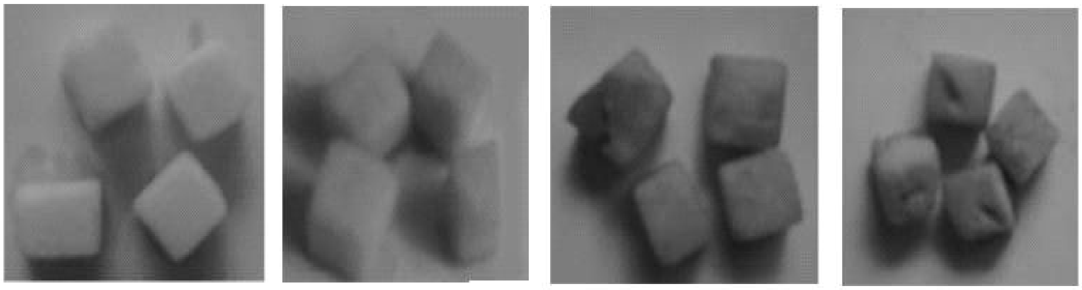


Fig. 2: Changes observed in PU foam cubes at 50°C using DEG, when it is sampled at 30, 60, 90 and 120 minutes

Variation of hydroxyl value at different time interval and temperature for PEG

Fig. 3 shows that hydroxyl values were found to increase gradually up to 60 minutes at 50°C, and then it increases slightly between the time range from 60 to 90 minutes. Further at the same temperature (50°C) again, the hydroxyl values increases gradually up to 150 minutes reaction time. Almost same behavior was observed at 100°C. The only difference is that at higher temperature (100°C), the hydroxyl value increases significantly from 60 minutes. It indicates that depolymerization of PU foam is comparatively faster at higher temperature.

Variation of hydroxyl value at different time interval and temperature for DEG

It was observed that in the solvent DEG, the hydroxyl value increases gradually up to 60 minutes reaction time at both the temperatures 50°C and 100°C (Fig. 4). But between 60 to 90 minutes, increment in hydroxyl value was little, further the hydroxyl value increases gradually at both temperatures up to 150 minutes reaction time. However, it was observed that at higher temperature of 100°C, increase in hydroxyl value was significant, and depolymerization in DEG was more at higher temperature. Figs. 3 and 4 reveal that hydroxyl value in the solvent at both the temperatures in PEG was more than DEG; this is because of the higher molecular weight of PEG having initially higher number of hydroxyl groups of solvent PEG.

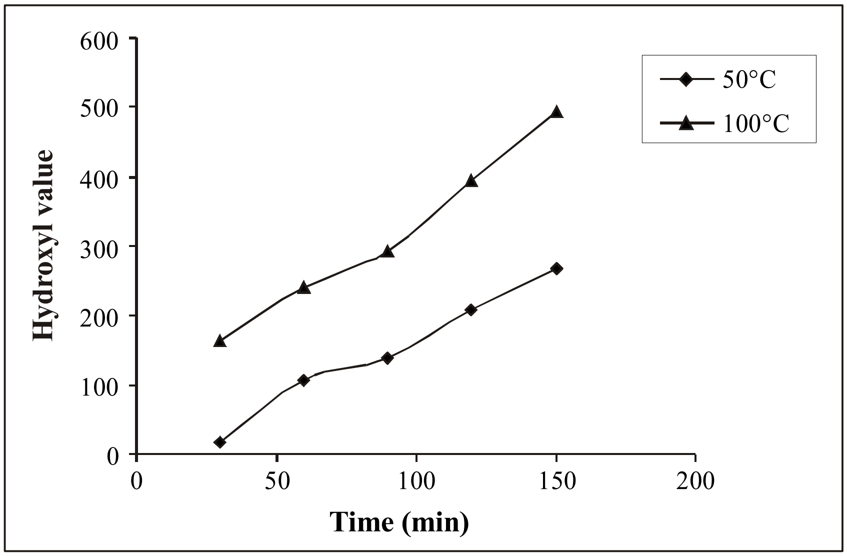


Fig. 3: Variation of hydroxyl value at different time intervals and at temperatures of 50°C and 100°C for PEG solvent

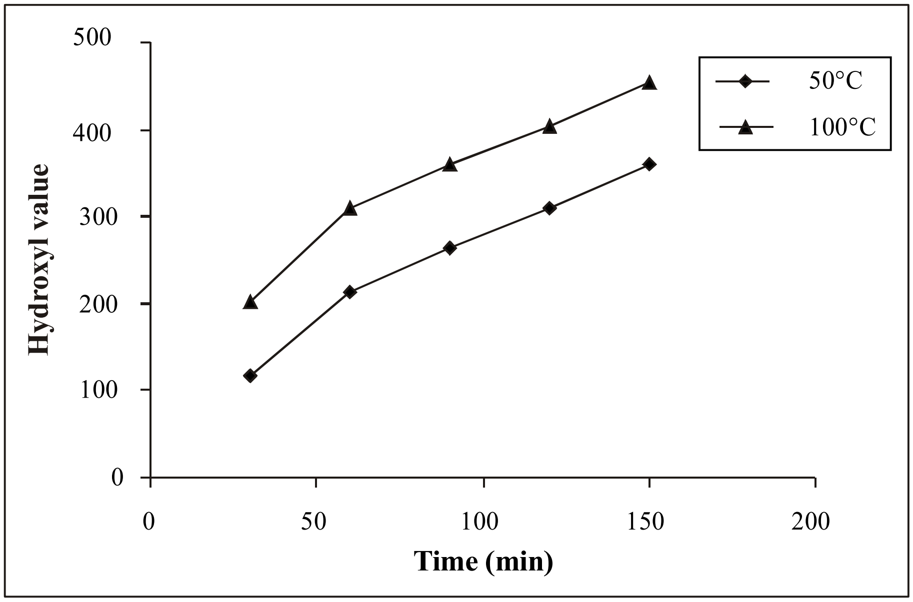


Fig. 4: Variation of hydroxyl value at different time intervals and at temperatures of 50°C and 100°C for DEG solvent.

Dissolution times in the solvents PEG and DEG

A Simple experimental technique for the measurement of dissolution time in the solvents PEG, EG and DEG was used. The cubes of PU foam of the dimension of 1 cm x 1 cm was kept immersed in the solvents. Table 2 shows that PU foam dissolution time in PEG and DEG in presence of catalyst sodium hydroxide at 200°C is very short (3 minutes). However at lower temperature of 150°C, the dissolution time was comparatively longer and found to be 15 minutes in DEG and 50 minutes in PEG. Thus, it has been observed that dissolution in DEG is faster than PEG, due to its molecular weight and density.

Table 2: Dissolution time and hydroxyl value of PU foam in PEG and DEG at temperature of 150° and 200°C

Temperature (°C)	PEG		DEG	
	Time (min.)	Hydroxyl value (mg KOH/g)	Time (min.)	Hydroxyl value (mg KOH/g)
150	50	920	15	858
200	3	993	3	942

The dissolution of PU foam in different solvents was due to its depolymerization, as indicated by the hydroxyl values. Significant increase in hydroxyl value indicates greater degree of depolymerization and shorter dissolution time.

Variation of hydroxyl value at different temperatures

Fig. 5 shows that variation of hydroxyl value at definite quantity of catalyst (6 g) and specific time (30 minutes) between the temperature ranges from 50°C to 200°C. It is evident from the figure that the increment in hydroxyl values from 50°C to 100°C is very small, further after 100°C hydroxyl value increases drastically up to 150°C. Hence maximum depolymerization was found to occur between 100°C and 150°C, after 150°C the hydroxyl value remains almost constant, indicating slight depolymerization between the ranges of temperature from 50°C to 100°C and 150°C to 200°C. The temperature range between 100°C to 150°C was found to be optimum for higher degree of depolymerization of PU foam.

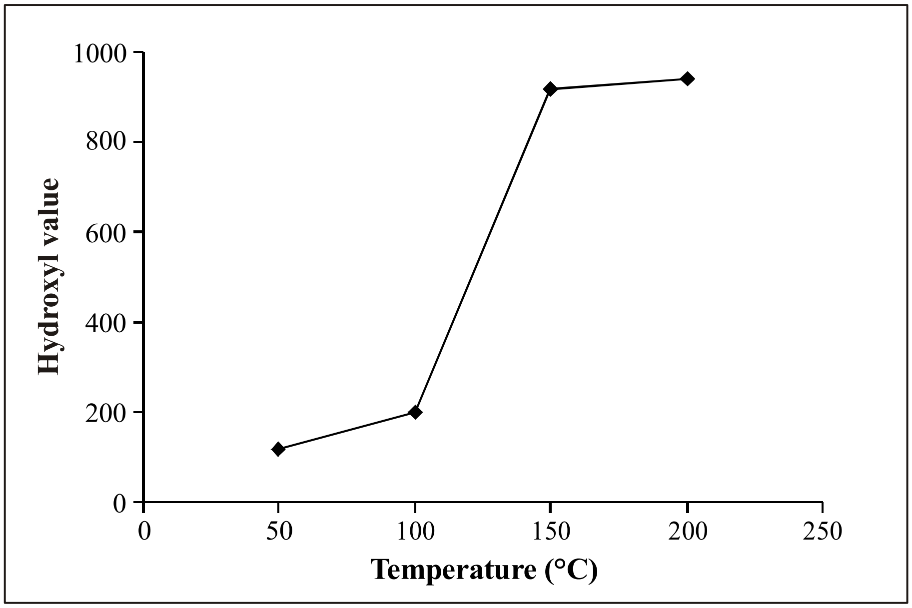


Fig. 5: Variation of hydroxyl value at different temperature and at specific time (30 minutes) and quantity of catalyst for DEG

Kinetics of depolymerization of PU foam

PU foam depolymerized to oligomers with terminal hydroxyl group. Therefore, concentration of PU foam depolymerized at any time could be measured by measuring the hydroxyl value after different time intervals. Hydroxyl value at zero time is $[HV]_o$. The hydroxyl value after definite reaction time is $[HV]_t$. Hydroxyl value at infinity time i.e., after completion of reaction is $[HV]_\infty$

The integrated rate law for first order kinetics of depolymerization of PU foam is given as -

$$k = \frac{2.303}{t} \log \frac{C_0}{C_t} \qquad \ldots(2)$$

Where C_o = initial concentration in terms of hydroxyl value, which is $[HV]_\infty - [HV]_o$ and C_t is the concentration of the depolymerized product in terms of hydroxyl value could be $[HV]_\infty - [HV]_t$ and hence, equation (2) reduced to -

$$k = \frac{2.303}{t} \log \frac{[HV]_\infty - [HV]_t}{[HV]_\infty - [HV]_o} \qquad \ldots(3)$$

Equation (3) is used to calculate velocity constant of depolymerization of PU foam on the basis of measurement of hydroxyl value.

Dissolution due to depolymerization of PU foam

The dissolution time for PU foam by glycolysis using solvents PEG and DEG was examined by performing a simple experimental procedure. After dipping the cubes of PU foam of the dimension 1 cm x 1 cm were heated at the different temperatures in presence of catalyst sodium hydroxide. The time of dissolution of PU foam was recorded at that specific temperature. Figs. 6 and 7 give relationship between the logarithm of the PU dissolution time and reciprocal temperature of the glycolysis (1/T). It was evident from the straight line nature of curve, that the dissolution by glycolysis obeys the Arrhenius law. From Figs. 8 and 9 the calculated energy of activation (*Ea*) was found to be 52.82 KJ mol^{-1} and 66.78 KJ mol^{-1}, respectively for DEG and PEG. Similarly, the rate constants calculated were found to be 1.18×10^{-4} mol^{-1} and 3.39×10^{-5} mol^{-1}, respectively for DEG and PEG, which clearly indicates that glycolysis of PU foam proceeds at a faster rate in DEG.

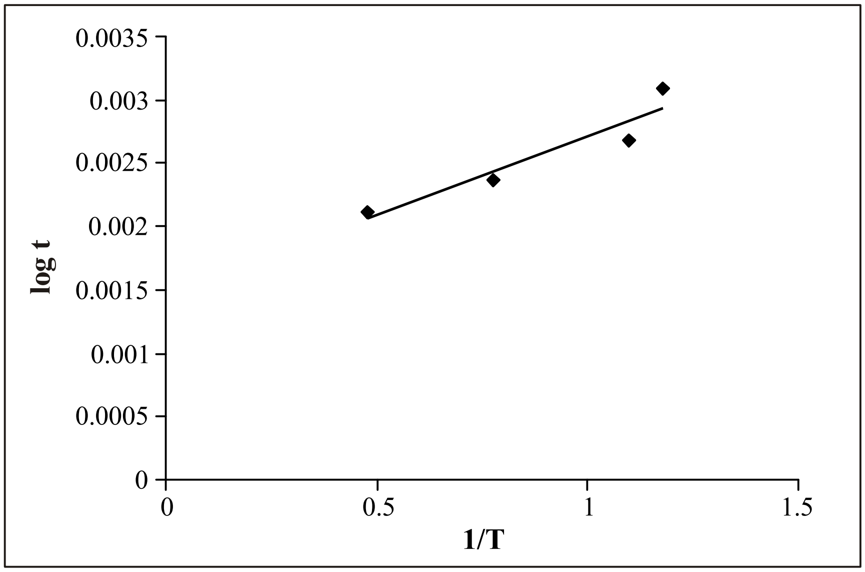


Fig. 6: Relationship between logarithm of PU foam dissolution time log t and reciprocal of temperature T for DEG

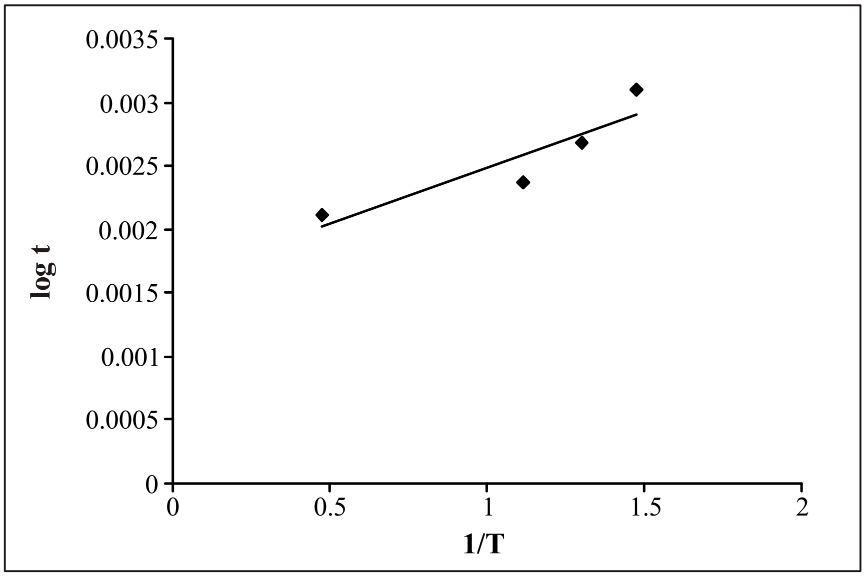


Fig. 7: Relationship between logarithm of PU foam dissolution time log t and reciprocal of temperature T for PEG

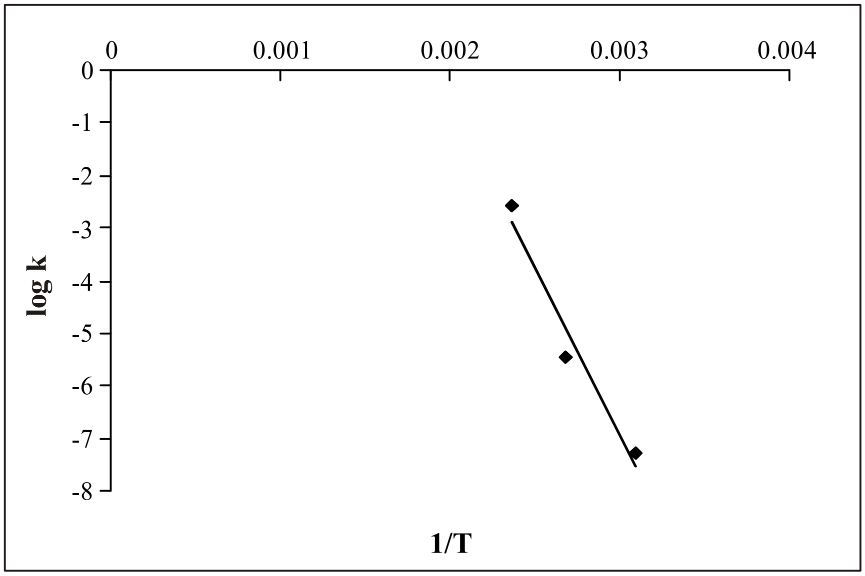


Fig. 8: Arrhenius plot of glycolytic depolymerization of PU foam for 30 minute reaction time using DEG for glycolysis

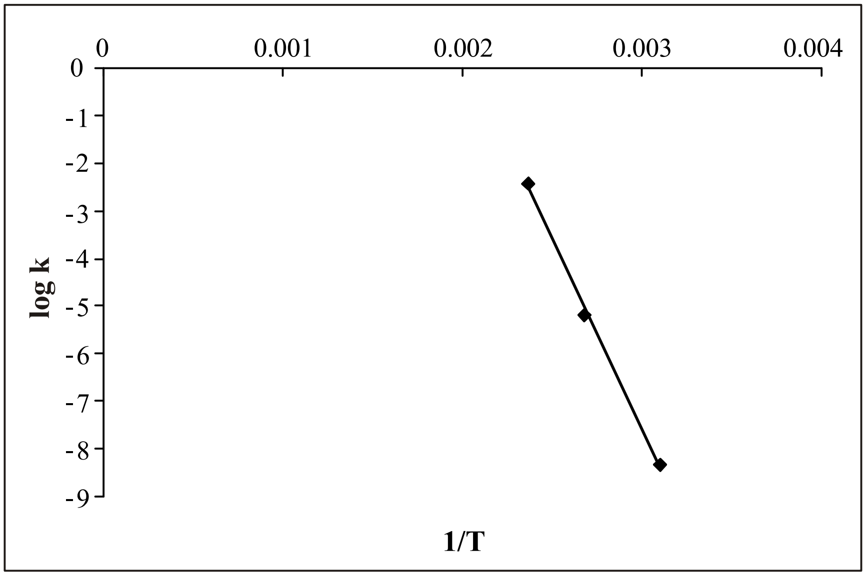


Fig. 9: Arrhenius plot of glycolytic depolymerization of PU foam for 30 minute reaction time using PEG for glycolysis

CONCLUSION

The following conclusions can be derived from these investigations -

(i) The depolymerization of PU is negligible in temperature range of 50-100^{0}C.

(ii) The depolymerization of PU increases proportionately with increase in quantity of catalyst.

(iii) The depolymerization of PU begins at 140^{0}C and increases to the maximum with increase in temperature up to 200^{0}C.

(iv) At the same reaction conditions with reference to temperature and quantity of catalyst added, PU dissolves at faster rate in DEG i.e., solvent with low molecular weight.

(v) The velocity constants were found to increase proportionately with increase in temperature.

(vi) The frequency factor (*A*), energy of activation (*Ea*) and rate constant of reaction were found to be 1.86 x 10^5 s^{-1}, 52.82 KJ mol^{-1} and 1.18 x 10^{-4} mol^{-1} for DEG, respectively as calculated on the basis of amine value.

(vii) The first order mathematical model proposed on the basis of hydroxyl value fits best to the depolymerization of PU foam verified by identical values of energy of activation (*Ea*) and rate constants at various temperatures.

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