

Chemical Recycling of Polyamide waste

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Abstract— Plastic have now emerged as one of the more essential materials for many major industrial transformational over the worlds. The changes and convenience offered typically by polymer blends, natural and synthetic fibres, reinforced composite, hybrid composite etc. Due to this everywhere use of polymer is increased. The excess use of polymer creates lot of polymer waste and is responsible for environmental pollution. The major bulk of the wastes of polyethylene terephthalate, polyethylene, polyamide and other polymers is either buried in the ground or burned, which is economically wasteful and ecologically hazardous. To overcome this reuse, recycling of polymer is must.

Dissolution and degradation processes are studied for recycling of polyamide waste. Different solvents such as dimethyl sulphoxide, dimethyl formamide, formic acid and p-cresol were undertaken for degradation of polyamide waste. Formic acid is found to be excellent for the degradation. These developed degradation process reduce the environmental pollution up to certain extent. The kinetic parameters such as order of the reaction (First), reaction rate constant (10^{-2}min^{-1}), activation energy ($17.442 \text{ k J mole}^{-1}$) and frequency factor (44.39 min^{-1}) were investigated by four batch wise heating. Ostwald viscometer method was used to determine the molecular weight of the polyamide waste and it was found to be 1.107×10^3 .

KEYWORDS: *Polymer recycling, Polyamide waste, Activation energy, Order of reaction.*

1. INTRODUCTION

Plastic is manmade materials which can be made into any form. There are many uses of plastics in human life however now a days plastics are a major source of solid waste pollution. The major bulk of the wastes of polyethylene terephthalate, polyethylene, polyamide and other polymers is

either buried in the ground or burned, which is economically wasteful and ecologically hazardous [1]. Polyamide now a days, mostly used in the form of carpet and engineering equipments. The carpet production also generates a substantial amount of waste in the form of trimming and cuts which typically amount to 12% of the total production [2]

There are four different techniques involved for Effective Waste Management, commonly referred as four "R" Reuse, Reduce, Recycle and Recover. Why to use Recycled Plastic? Protects resources, reduces unnecessary waste, reduced disposal cost, reduces land filling costs and creates new jobs. The best advantage of recycling of plastics is to create an employment by different processes and its types. A plastic degrades slowly under the effect of wind, sun and rain. Plastics waste is one of the most objectionable kinds as litters. It lies around; it becomes coated with objectionable waste and blocks the drainage systems.

Any process of recycling that places a value upon this material, so that there is financial advantage is preserving it rather than the discarding it, such process is to be welcomed. The benefit is greater in poor, urban areas where even small earning opportunities will be seized. As these are the districts where municipal cleaning frequency is least. By implementing a beneficiary scheme in such areas will boost the poor people to earn a lot through collection, sorting of plastic waster for recycled. Land filling due to plastic waste creates environment pollution problem. The recycling process can be achieved through different stages, such as collection, sorting and cleaning material which are labour intensive and require little capital equipments. The work is suitable for those who have little skill and the sorting and cleaning may be

done by people with certain sort of disability. Disposal of plastics to land fill is avoided by eco-friendly chemical recycling [3-4] by hydrolysis, aminolysis, glycolysis etc. In present study the degradation of polyamide waste, viscosity molecular and kinetics parameters has been studied

MATERIAL AND METHODS

Material: Analytical grade chemical such as sodium hydroxide, formic acid, Demethyl sulphoxide, Dimethyl-formamide, P-cresol supplied by S.D. fine chemicals, were used as received. Polyamide waste sample obtained from the Ashwini Engineering Works, MIDC, Jalgaon (MS).

Degradation Kinetics of Polyamide: 1 g of polyamide waste sample was taken in different beakers of capacity 100 ml containing various solvent such as Dimethyl Sulphoxide (DMSO), Dimethyl formamide (DMF) and p-cresol. After definite timing intervals, the degree of degradation is recovered by measuring the residual weight of the sample. The kinetics of degradation (dissolution) of polyamide waste in formic acid has been studied by measuring polyamide wastes after definite reaction time. Degradation of polyamide by hydrolysis was experimentally studied by taking 1 g of polyamide sample in three neck flask of capacity 250 ml containing 1 g of NaOH facilitate, with Condenser. The flask was heated for various

time intervals after definite time interval the residual weight of sample is measured by using chemical balance.

Thermodynamics: 1 g of polyamide sample was taken in formic acid solvent. The dissolution was observed at various temperatures ranging from 30⁰C to 90⁰ C. Residual weights after dissolution were recorded for every 15 minutes dissolution time.

Molecular Weight Determination: Viscosity average molecular weight of polyamide waste was determined by using Ostwald Viscometer. The flow time of various concentration of polyamide waste prepared in formic acid was recorded. The intrinsic viscosity (intercept =0.7088) of the graph was used to calculate the average molecular weight by using the formula, $[\eta] = K M^a$. M is the molecular weight of polymer obtained as 1.107×10^3

RESULTS AND DISCUSSIONS:

Degree of dissolution (Degradation):

The present study is based on the simple experiments carried out to observe the dissolution of polyamide waste into the various solvents such as p-cresol, Dimethyl sulphoxide, Dimethyl formamide, formic acid, there is absolutely no dissolution (degradation) in dimethyl formamide. However 100% dissolution was observed in formic acid solvent. Table 1.1 shows that

Table 1.1 Dissolution time of polyamide waste sample in various solvent

Dissolution time (min)	Dissolution percentage in Solvents			
	DMSO	p-cresol	Formic acid	DMF
05	00	00	20.58	00
10	00	00	34.50	00
15 and 30	00	00	100	00
120	00	27.74	100	00
1440	00	90.41	100	00
4320	01	100	100	00

100% degradation was achieved in 15 minutes and 4320 minutes for formic acid and p-cresol solvents respectively. It is evident from this observation that formic acid is an effective solvent for the degradation of polyamide waste. The linear increase in percent degradation was observed for both the solvents formic acid and p-cresol;

Table1.1 also shows that no degradation was observed up to 1440 minutes dissolution time for the DMSO. It was also observed that practically there is no degradation of the sample in the solvent DMF even for longer time.

Alkali hydrolysis of polyamide waste: It was observed that for the alkali hydrolysis of polyamide waste at atmospheric pressure and elevated temperature of about 100°C that there is absolutely no degradation. However literature reviews indicates that such a alkali hydrolysis is possible only at high pressure and temperatures [3]. Thus high pressure autoclave has been recommended to carry out this reaction process [5-6].

Kinetics of degradation of polyamide waste: The rate constants of reaction were determined using first order kinetic equation,

$$k = \frac{1}{t} \ln \frac{W_0}{W_t} \dots\dots\dots(1.1)$$

Where, W_0 is the initial weight of polyamide waste in grams and W_t is the weight of the reactant left at time 't' in grams.

The values obtained for 'k' using equation (1.1) at various temperatures are reported in Table 1.2. The temperatures are 30, 50, 70 and 90°C and the corresponding rate constant obtained are 4.1×10^{-2} , 7.1×10^{-2} , 10.84×10^{-2} and $12.54 \times 10^{-2} \text{ min}^{-1}$ respectively.

Table 1.2 Variation of rate constant with temperature

Temperature (T°K)	Rate constant (k)	ln k	1/T
303	4.1×10^{-2}	-3.1942	3.300×10^{-3}
323	7.1×10^{-2}	-2.6450	3.095×10^{-3}
343	10.8×10^{-2}	-2.2219	2.915×10^{-3}
363	12.5×10^{-2}	-2.0762	2.754×10^{-3}

It indicates that as the temperature increases the rate constant also increases. The values of 'k' are constant is observed to be constant using first order reaction rate expression hence the reaction shows first order kinetics. The degradation reaction is first order with rate constant of order of 10^{-2} min^{-1} .

Percent conversion of degradation reaction: The degradation process leads to the conversion of polyamide waste in to monomer or oligomers. The percent conversion increases as temperature increases. It was observed that maximum conversion (84.86%) was achieved at 90°C for 15 min dissolution time. Thus 90°C, temperature is

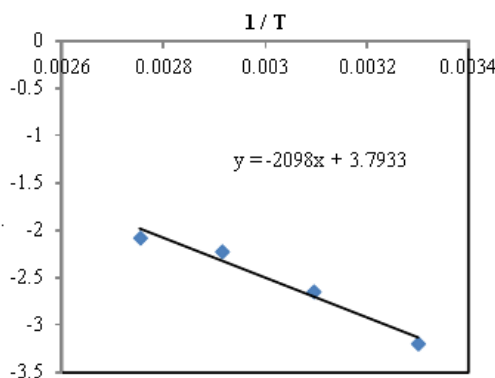
found to be optimum temperature for the degradation process. According to Arrhenius equation,

$$k = A e^{-E_a/RT} \dots\dots\dots(1.2)$$

Where, the symbols have their usual meaning.

The equation (1.2) is useful to determine the energy of activation and Arrhenius constant by plotting the graph of ln k against 1/T as shown in Fig. 1.1.

Figure 1.1 Variation of ln k against 1/T



The slopes and intercept of the Arrhenius plot were 2098 and 3.793 respectively. The energy activation and Arrhenius constant obtained by using these values were 17.442 k J mole and 44.39 min^{-1} respectively.

CONCLUSION:

The dissolution of polyamide waste is of first order with reaction rate constant in the order of 10^{-2} min^{-1} . The energy of activation and frequency factor were found to be 17.442 kJ mole⁻¹ 44.39 min⁻¹ respectively. The average molecular weight of the polyamide waste sample was found to be 1.107×10^3 by Ostwald viscometer method using appropriate equation.

Among all the various solvents used the formic acid is found to be the best solvent dissolution (degradation) of polyamide waste.

There is absolutely no degradation is observed in dimethyl formamide while slight degradation is seen in case of dimethyl sulphoxide.

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Synthesis of Polypyrrole/Graphene Oxide 2-D Nanostructures Using Swollen Liquid Media Crystal and Their Application as Supercapacitor

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Graphene oxide (GO) based nanocomposites and polypyrrole (PPy) were prepared through in-situ chemical polymerization in surfactant based “soft templates”. The PPy and graphene oxide based nanocomposites were synthesized in swollen lamellar mesophase based on anionic surfactants (sodium dodecyl sulfate). The surface morphology of synthesized PPy and GO-PPy is 2-D nanostructures like nanosheets was observed using FE-SEM and AFM techniques. Such uniform 2-D nanostructures of PPy and GO-PPy have superior conductivity afforded as well as capacitance. The specific capacitance of GO-PPy is 440 F/g at a 10 mV/s was achieved.

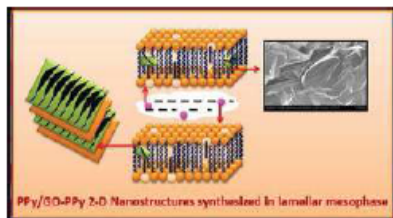


Figure 1. Graphical Abstract

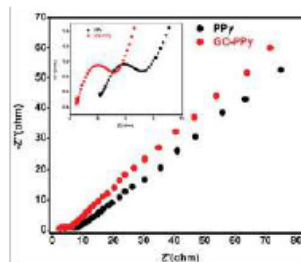


Figure 2. Nyquist impedance plot of a) PPy and b) GO-PPy

Electrochemical supercapacitors have been major focus of research for the invention of stored energy with high power density. Such devices yield properties which are explored in various applications such as hybrid electric vehicles, satellites, cell phones, personal electronics and industrial power back-up systems [1]. Hence, supercapacitors have two parts for stored energy, electrical double layers capacitance (EDLC) and the pseudocapacitance. Electrical double layer capacitance (EDLC) including the carbon nanostructures like graphene and carbon nanotubes (CNTs). Pseudocapacitance stored the energy using fast redox reactions between the electrodes and electrolyte i.e. conducting polymers and metal oxides.

Herein, the nanoscale synthesis of PPy and graphene oxide/polypyrrole (GOPPy) 2-D nanostructures like nanosheets has been achieved using quaternary system such as (SDS-oil-water-co-surfactant) based swollen liquid lamellar mesophase for the first time. In-situ chemical oxidation polymerization reaction of PPy and GO-PPy 2-D yielded nanostructures using of ammonium persulfate as oxidant.

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