Scanning electron microscopic study of hazardous waste flakes of polyethylene terephthalate (PET) by aminolysis and ammonolysis

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ARTICLE INFO

ABSTRACT

Polyethylene terephthalate (PET) waste flakes were degraded with aqueous methylamine and aqueous ammonia, respectively at room temperature in the presence and absence of quaternary ammonium salt as a catalyst for different periods of time. The aminolysed and ammonolysed PET samples were investigated for the surface morphology with the help of scanning electron micrograph (SEM). It shows that the semi-crystalline PET waste samples reduce to monodisperse rods before fully degradation to the end products. The presence of the catalyst provides site for degradation of PET waste and enhances the rate of degradation. The SEM shows early developments of fissures in comparison to the one in absence of quaternary ammonium salt used as catalyst.

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1. Introduction

Some aromatic polyesters are biodegradable but PET waste is not biodegradable, thus, it will create environmental hazards if disposed in landfills [1]. Therefore, the only way of addressing the problem of disposal of post-industrial and post-consumer PET waste is through recycling [2]. Recycling may be defined as any activity involving reclamation, recovery or reuse of materials or articles. It also extends the service life of plastics. A striking feature of PET, which is on the environmental side, is that it is fully recyclable.

Extensive studies of various degradation reactions of PET have been reported [2]. Two kinds of methods of recycling known as mechanical [3] and chemical recycling [4] are used in recycling of PET waste. Most of the chemicals recycling methods include hydrolysis [5,6], alcoholysis [7,8] and glycolysis [9,10]. The chemical methods of recycling allow recovery of original monomers or other modified chemicals. These methods require tedious conditions of high pressure and high temperature.

Limited but significant contributions have been reported on the aminolysis and ammonolysis of PET waste by various workers [11–14]. Soni et al. [15] used methylamine, ethylamine and n-butylamine to the selective amminolysis of PET waste at room temperature. Soni et al. [16] have suggested that aminolysis with 99% hydrogen monohydrate degrades PET bottles, increases percent crystallinity of the residue and decreases molecular weight. Soni and Singh [17] reported the formation of terephthalamide and N,N'-dimethyl terephthalamide by the degradation of PET waste through aminolysis and ammonolysis using aqueous methylamine and ammonia, respectively at normal conditions of temperature and pressure.

In the present work, the PET waste was degraded by aminolysis and ammonolysis for different periods of time. The morphology of the end products of PET waste obtained after different lengths of time was studied with the help of scanning electrons microscopy.

2. Experimental

2.1. Materials and characterization

PET waste flakes as obtained from the industry were put into a hot water bath maintained at 70–100 °C to ensure the effective separation of PET flakes from other impurities. PET flakes so separated were washed thoroughly with distilled water and dried at 60 °C.

An aqueous solution of methylamine (40%, w/v), procured from M/s Central Drags House, New Delhi (India), laboratory grade and 40% (w/v) aqueous ammonia (sp. gravity 0.91), procured from M/s Qualigens, Mumbai (India), laboratory grade, were used for aminolysis and ammonolysis respectively.

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Table 1
Weight of unreacted PET and degraded product during aminolysis and ammonolysis in presence and absence of catalyst.

| No. of days	Weight of unreacted PET waste (g)				Weight of product (g)			
	Aminolysis		Ammonolysis		Aminolysis		Ammonolysis	
	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst
0	10.0	10.0	10.0	10.0	0	0	0	0
3	6.7	8.3	9.0	9.4	3.1	1.5	0.7	0.6
7	5.3	7.2	8.1	8.6	4.5	2.6	1.7	1.4
15	4.1	5.6	6.9	7.3	5.6	4.2	3.0	2.7
21	3.2	4.0	6.2	7.1	6.3	5.7	3.6	2.9
25	2.7	3.5	6.0	6.9	7.0	6.2	3.8	3.1
30	1.9	2.9	PET flakes get brittle		7.9	6.8	PET flakes get brittle	
45	0.0	1.3			9.4	8.4		

2.2. Preparation of sample

Polyethylene terephthalate waste is in the form of flakes size ranging from 1 to 2 cm. For the degradation of polyethylene terephthalate waste through aminolysis, the PET waste flakes were made to react with aqueous methylamine in properly sealed round bottom flask. A quaternary ammonium salt namely cetyl ammonium bromide was used as catalyst. The PET waste was subjected to degradation for different periods of time i.e. 3, 7, 15, 21, 25, 30 days. The PET flakes were separated and dried under vacuum at room temperature.

Similarly, in the ammonolysis of PET waste flakes, degradation experiments were carried out with aqueous ammonia solution. Dried PET waste reacted with excess of aqueous ammonia in the ratio of 1:10 w/v by weight at room temperature (40 °C) with continuous constant stirring. The degraded PET flakes were separated from the white precipitates. These PET flakes were washed with water and dried over vacuum [16].

2.3. SEM studies

SEM studies were done on TEOL JSM-840 scanning electron microscope. All of the end products obtained by aminolysis and ammonolysis of PET waste after different periods of time were gold plated with 22 carat gold (400 μm thickness coating) before subjecting the sample flakes to the heated source of electrons. The electron beam was moved over the sample surface and the electrons penetrated the material to a considerable depth. This gen-
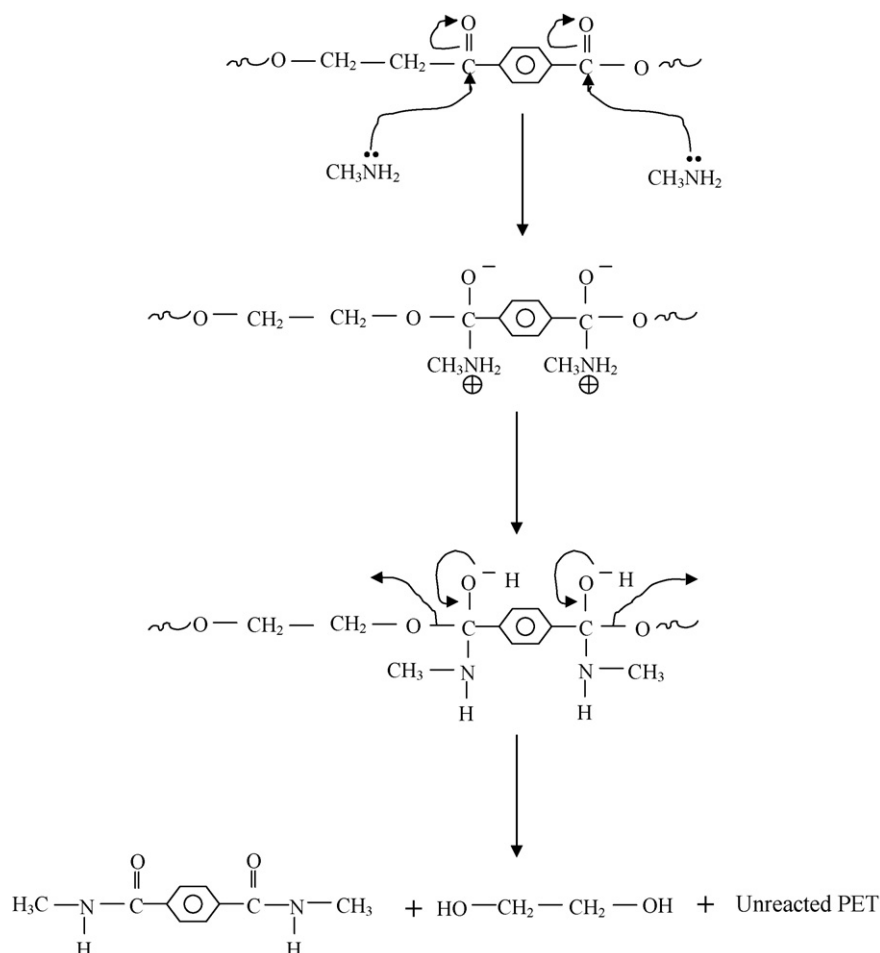
Scheme 1. Proposed mechanism for PET degradation by aminolysis in absence of catalyst.

erated image was photographed at magnification of 2000 time. The experiment was preformed both in the presence and absence of quaternary ammonium salt.

3. Results and discussions

### 3.1. Degradation of PET waste through aminolysis and ammonolysis

Aminolysis and ammonolysis of PET waste give only one product through out namely N,N′-dimethyl terephthalamide and terephthalamide, respectively, for various lengths of time i.e. 3, 7, 15, 21, 25, 30 and 45 days. This indicates that at every stage of the reaction same mechanism is followed.

It is pertaining to note that in the case of ammonolysis of PET waste, it was observed that after 30 days the PET flakes become brittle in presence and absence of catalyst therefore no further changes in the micrographs were observed. The brittleness of the PET waste was in such a state that it was not possible at all to separate the untreated PET waste from the mixture and that is why the untreated PET waste could not be weighed.

3.2. Proposed mechanism for PET degradation via aminolysis/ammonolysis

Aminolysis and ammonolysis of PET waste gave N,N′-dimethyl terephthalamide and terephthalamide as end products as per the following reaction:

a) Aminolysis

N,N' –Dimethylterepthalamide
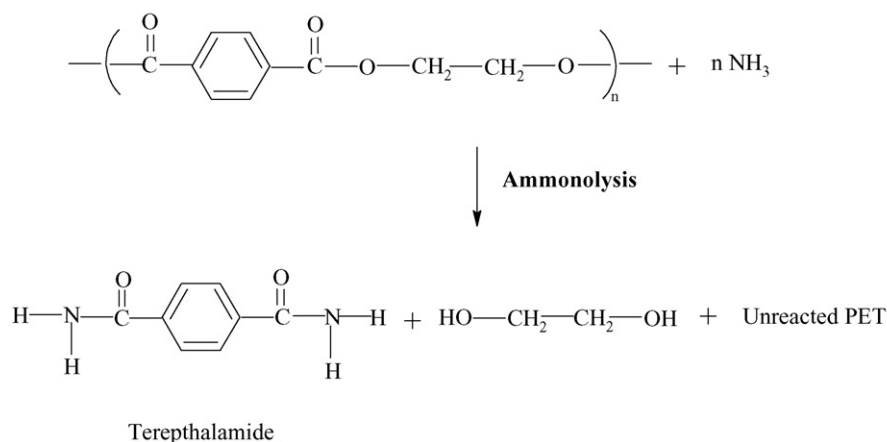
b)Ammonolysis

Terepthalamide
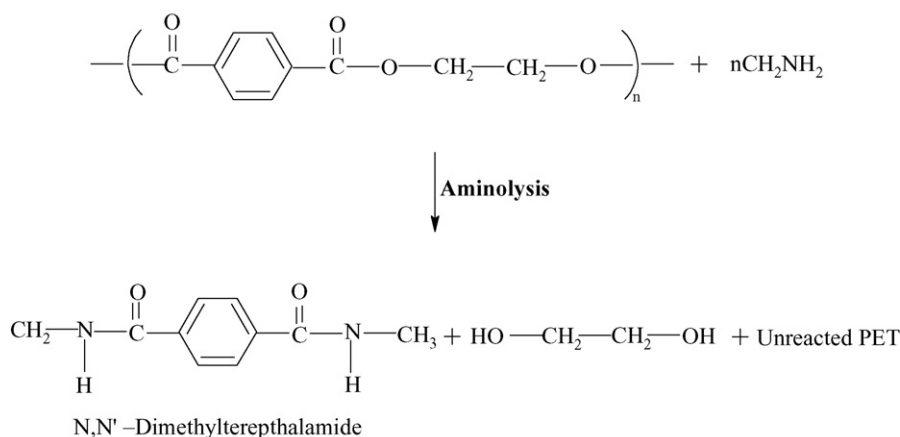
Table 1 summarizes the weight of PET waste left unreacted and that of the degraded product so formed in presence and absence of catalyst at different lengths of time. This reveals that in absence of catalyst even after 45 days of reaction time, 13% by weight of PET waste was left unreacted while in presence of catalyst, the reaction completes after 30 days and after 45 days, no PET waste flakes were left unreacted.

This confirms the formation of single product through out the reaction, complete degradation of PET flakes, and increased rate of degradation in presence of catalyst and absence of any side reaction.

There are two different phases involved in the both aminolysis and ammonolysis: one is aqueous (methylamine/ammonia) and the other of solid (polymer). Aqueous phase is expected to carry a neculeophile. Methylamine and ammonia are much weaker acids than water. Since acids could hardly catalyze the reaction, this reaction does not occur by an electrophilic mechanism but occurs by a nucleophilic mechanism, and so the rate of degradation reaction is slow in nature. But it cannot be concluded that whether the reaction occurs by random scission or by unzipping method. If degradation occurs by random scission, same product should not

be obtained at different lengths of time, and also the possibility of formation of other terephthalamides cannot be ruled out. Since we have obtained same white solid and got 100% pure terephthalamides, it therefore, cannot be concluded that the reaction occurs by random scission. If degradation occurs by unzipping method, degradation should have started at one end and finished at the other end. But since amorphous region of PET, undergoes degradation more rapidly than the crystalline region, unzipping also seems to be unreasonable. It can be concluded that both random and unzipping mechanism of degradation are followed simultaneously.

3.2.1. Proposed mechanism for PET degradation by aminolysis in absence of catalyst

Methylamine acts as a nucleophile and attacks PET at the electron deficient center C–O. Scheme 1 gives a proposed picture of PET degradation by aminolysis in absence of catalyst.
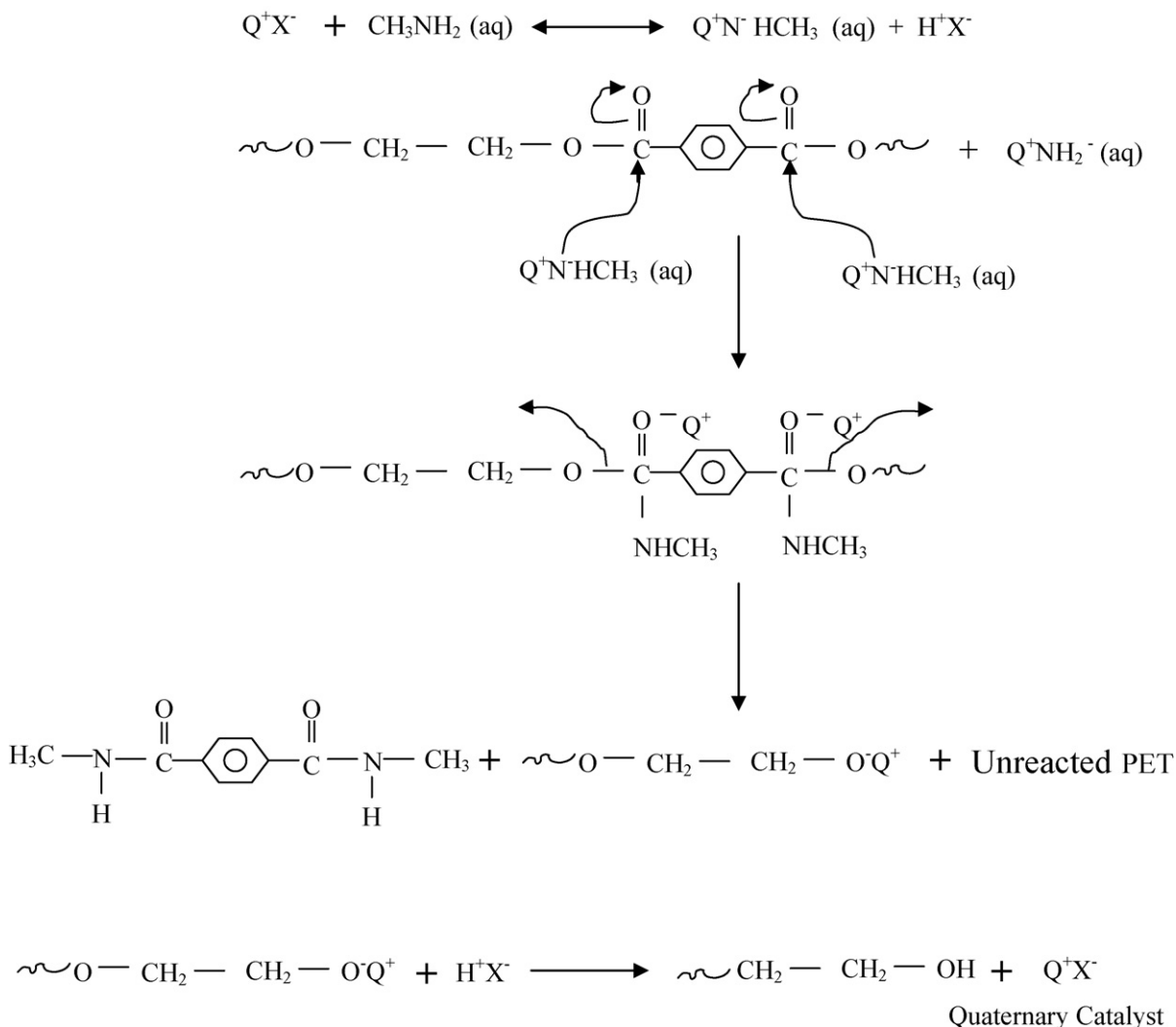
3.2.2. Proposed mechanism of PET degradation by aminolysis in presence of catalyst

When quaternary salt (Q$^+$X$^-$) is added to the mixture, it is expected to exchange its anion with the excess of nucleophile in the aqueous phase. Scheme 2 gives the proposed mechanism for PET degradation by aminolysis in presence of catalyst. QN$^+$H$^-$ attacks the polymer and displacement occurs with the product formation.

3.3. SEM studies on the degradation product of PET waste by aminolysis

Fig. 1(a) shows SEM micrograph of PET waste flake at magnification of 2000 before subjecting it to degradation by aminolysis and ammonolysis. It presents a smooth and continuous flake structure. It reveals that PET is more crystalline in nature than amorphous, and that the amorphous regions are scattered in between the oriented chains. SEM studies on the degradation products of PET waste by aminolysis SEM micrographs of PET flake degraded for 3 days with aqueous methylamine in presence and absence of catalyst. The SEM micrograph for the PET chips subjected to degradation by methylamine shows fissures of length ranging from 5 to 10 μm. Initially, methylamine selectively attacks amorphous region leaving behind crystalline PET. After certain periods of time both crystalline and amorphous regions are attacked. This observation is in agreement with the earlier reported literature [11], which states that

Scheme 2. Proposed mechanism of PET degradation by aminolysis in presence of catalyst.
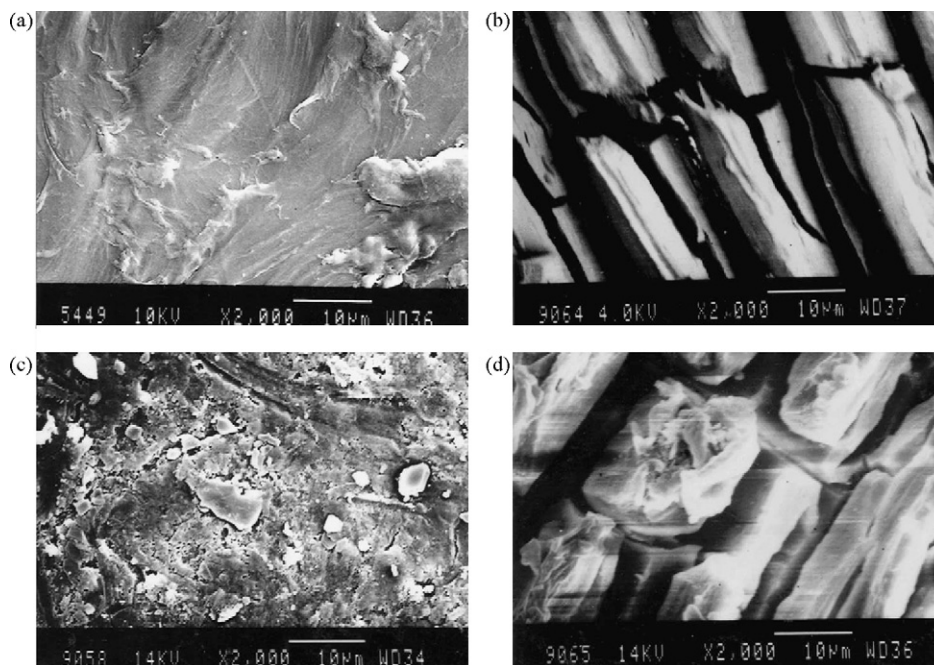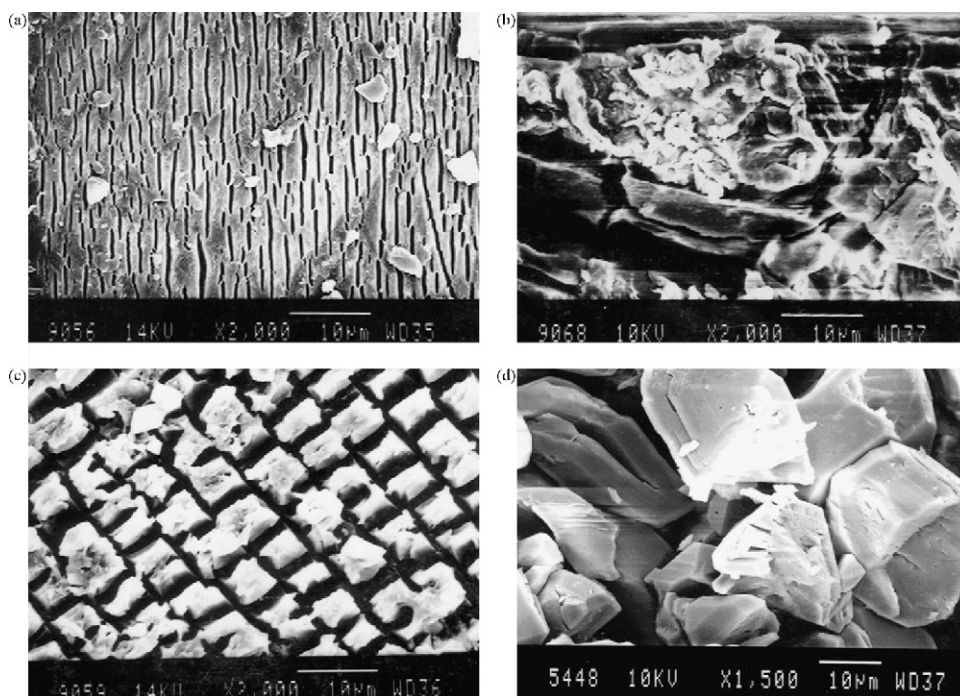
Fig. 1. (a) SEM of PET flakes. (b) SEM of PET flakes degraded for 7 days by amminolysis in the presence of catalyst. (c) SEM of PET flakes degraded for 7 days by amminolysis in the absence of catalyst. (d) SEM of PET flakes degraded for 21 days in the presence of catalyst.

methylamine, is selective enough to separate the two morphological phases of PET. The amorphous region of PET degrades much faster, and the effect has been found to be more pronounced when a quaternary salt is used as a catalyst. This shows cuts all over the surface of PET while no fissures are there in SEM micrograph of PET flake degraded for even after 3 days by aminolysis in absence of catalyst indicating that the reaction is much slow in the absence of catalyst. These fissures get widen in SEM micrograph of PET flake degraded for 7 days by aminolysis of PET waste in presence of cat-

alyst. It presents more regular cuts all over the surface of PET as shown in Fig. 1(b), indicating that the whole region of PET is under degradation. While SEM micrograph of PET flake degraded for 7 days in the absence of catalyst shows that a little portion of PET surface has started degrading here and there and still no fissures appears as shown in Fig. 1(c).

These fissures get more widen in SEM micrograph of PET flakes degraded for 15 days by aminolysis of PET waste in presence of catalyst. After 15 days of degradation the lamellar morphol-

Fig. 2. (a) SEM of PET flakes degraded for 21 days by amminolysis in the absence of catalyst. (b) SEM of PET flakes degraded for 30 days by amminolysis in the presence of catalyst. (c) SEM of PET flakes degraded for 30 days by amminolysis in the absence of catalyst. (d) SEM of the product obtained after degradation of PET waste flakes with aqueous methylamine both in the presence and absence of catalyst.
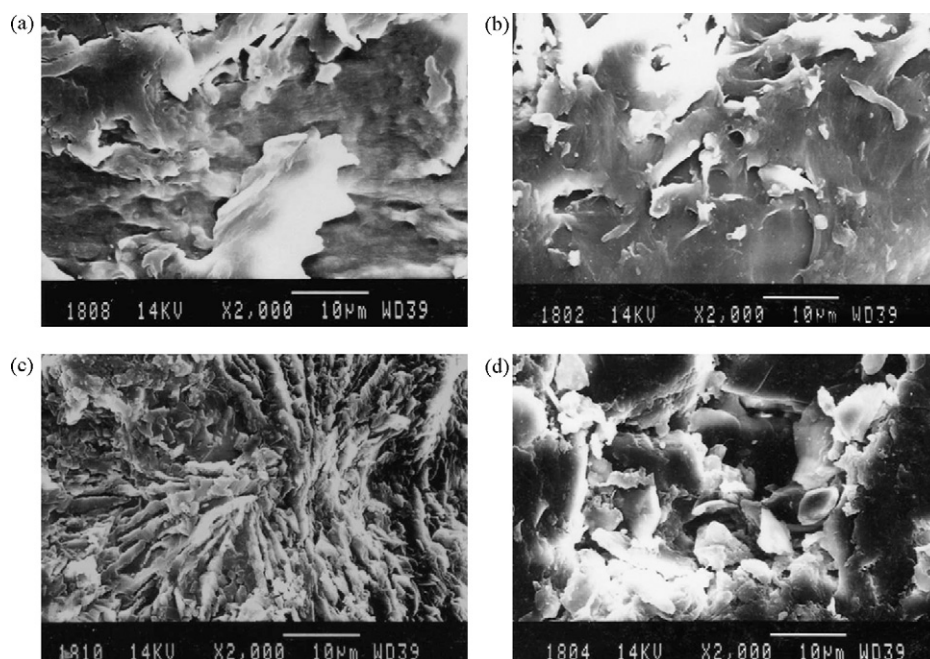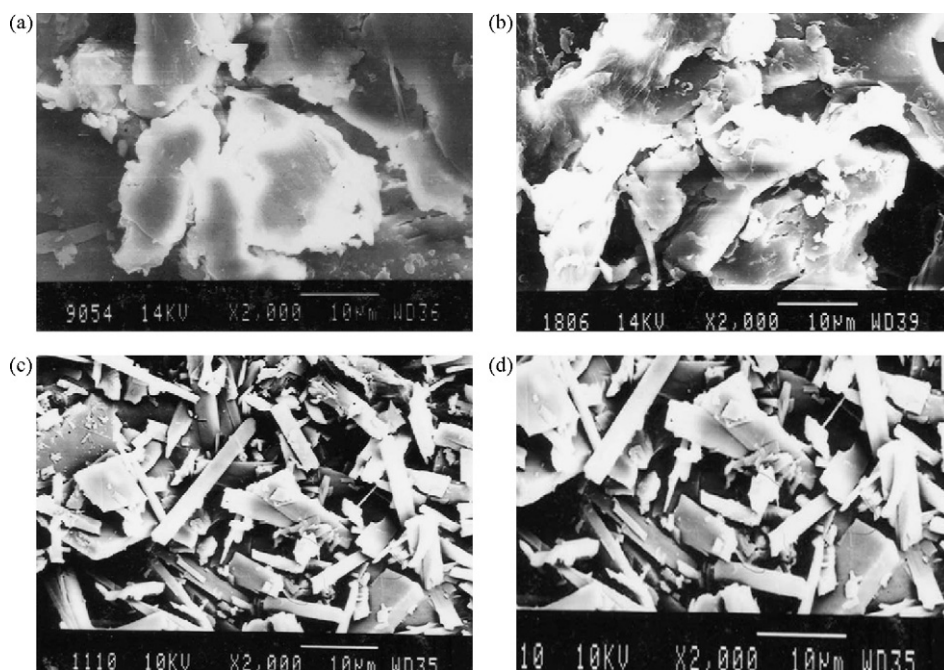
Fig. 3. (a) SEM of PET flakes degraded for 7 days by ammonolysis in the presence of catalyst. (b) SEM of PET flakes degraded for 7 days by ammonolysis in the absence of catalyst. (c) SEM of PET flakes degraded for 21 days by ammonolysis in the presence of catalyst. (d) SEM of PET flakes degraded for 21 days by ammonolysis in the absence of catalyst.

ogy of PET flake starts reducing to crystals of distinct shape as clear from the SEM micrograph. SEM micrograph of PET degraded for 15 days in absence of catalyst now show appearance of fissures of about 3–12 μm, which are observed after 3 days in presence of catalyst. This clearly indicates that the rate of degradation of PET flake in absence of catalyst is much slower than in the presence of catalyst. It is apparent from SEM micrograph that these fissures get more and more widen when PET flakes were degraded for 21 days. The SEM micrographs of PET

flake degraded for 21 days in presence of catalyst show that the degradation of PET flake is near completion as evident from Fig. 1(d), while the micrograph taken in absence of catalyst after 21 days presents fissures all over the surface of PET as shown in Fig. 2(a).

Comparison of micrographs (Fig. 2(b) and (c)) for degradation of PET after 30 days under two different conditions clearly shows that though rate of degradation has almost equalized, still degradation of PET in presence of catalyst has an edge over the reactions

Fig. 4. (a) SEM of PET flakes degraded for 30 days by ammonolysis in the presence of catalyst. (b) SEM of PET flakes degraded for 30 days by ammonolysis in the absence of catalyst. (c) SEM of the product obtained after degradation of PET waste flakes with aqueous ammonia both in the presence of catalyst. (d) SEM of the product obtained after degradation of PET waste flakes with aqueous ammonia both in the absence of catalyst.

carried out without catalyst. It is apparent from Fig. 2(b) that PET degradation in absence of catalyst is also near completion.

After 45 days of PET degradation in presence of catalyst, no PET flakes remain while in absence of catalyst some of the PET flakes left unreacted. Fig. 2(d) shows SEM micrograph recorded at magnification of 1500, of the product obtained after degradation of PET with methylamine both in presence and absence of catalyst. Same micrograph was obtained under both the conditions i.e. in the presence of catalyst and in the absence of catalyst and therefore, only one micrograph is presented.

When PET waste flakes are exposed to methylamine environment in presence of quaternary ammonium salt, deep fissures develop and as the time progresses, these fissures further deepen and the long folded chains are reduced to short mono disperse rods. Though these observations are the same for the reactions carried out in absence of quaternary salt, yet initial rates of degradation are found to be much faster for the reactions carried out in presence of quaternary salt as catalyst.

3.4. SEM studies on the degradation product of PET waste by ammonolysis

After 7 days of degradation of PET waste in presence of catalyst and in the absence of catalyst the SEM micrographs show that degradation of PET waste is increased as shown in Fig. 3(a) and (b), respectively. It is apparent from the SEM micrograph of PET waste degraded by ammonolysis in the presence and absence of catalyst for 15, 21, 25 and 30 days that in ammonolysis whole mass is getting converted into the degraded products (Figs. 3(c), (d) and 4(a), (b)).

After 45 days SEM micrograph of product obtained after degradation of PET waste with aqueous ammonia both in the presence and absence of catalyst shows the complete degradation of PET waste into the degraded products as shown in Fig. 4(c) and (d), respectively.

SEM micrographs of PET flakes degraded in absence of catalyst reflect initially lower rate of degradation. Degradation of PET in absence of catalyst after 15 days is same as degradation of PET in presence of catalyst after 3 days. After 25 days, there were no significant changes in rate of reaction and the rate of degradation in the presence and absence of catalyst almost equalizes. After 45 days, only short brittle PET flakes remain, which can easily be crushed down. Same micrographs are obtained both in the presence and absence of catalyst as evident from Fig. 4(c) and (d), respectively.

When PET waste flakes are exposed to ammonia environment separately in presence and absence of catalyst, it is observed that the initial rate of degradation is faster in presence of a catalyst at all length of time in comparison to the degradation carried out without catalyst. Further, both in presence and absence of catalyst ammonia attacks simultaneously the amorphous and crystalline regions of PET, but its selectivity to separate the two morphological phases is very low in comparison to that of methylamine and may be attributed to the fact that the selectivity of a reactant depends on its nucleophilicity. Methylamine is a better nucleophile than

ammonia and therefore it is more selective in separating the two morphological phases in PET.

4. Conclusion

SEM studies carried out on aminolysed and ammonolysed PET waste flakes reflect that degradation occurs faster in the presence of catalyst than in the absence of catalyst. These studies reveal that the long polymeric chains in the semi-crystalline PET reduce to monodisperse rods and the fissures on the surface of PET deepened with time. Amorphous portion is removed at a faster rate, and there is a marked increase in the crystallinity of the residue towards completion of the reaction.

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