# A Study on the Biodegradability of Polyethylene Terephthalate Fiber and Diethylene Glycol Terephthalate

**Jianfei Zhang, Xiaochun Wang, Jixian Gong, Zhenya Gu**

*College of Material Science and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300160, People's Republic of China*

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**ABSTRACT:** The degradation of diethylene glycol terephthalate (DTP) and polyethylene terephthalate fiber (PET fiber) by microbes and lipase was studied. The HPLC method was used to determine the degradation ratio and degradation rule of DTP. Greater than 90% DTP was degraded by microbes in 24 days and 40% by lipase in 24 h. The degradation of DTP can be described by the first-order reaction model. Although the biodegradation ratio of PET fiber was still weak, we demonstrated with SEM micrographs and HPLC analysis that microbes and lipase could act on the PET fiber and there were some cracks on the surface of the fiber.
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**Key words:** microbe; lipase; biodegradation; DTP; PET fiber; environment

## INTRODUCTION

With the rapid development of polyethylene terephthalate (PET) and its wide use in industry, there is a substantial fraction by volume added to the waste stream every year, which causes an environmental issue, since PET is highly resistant to atmospheric and biological agents. Therefore, PET is a noxious material from a global environmental and ecological standpoint.[1–3]

Currently, the handling methods of PET and other polymer wastes involve burying, burning, and recycling.[4] But, as regards environmental protection, these methods have many shortcomings and cannot address PET waste pollution from the source. Burying is the simplest and oldest method, but it has produced many problems such as occupying land, polluting groundwater, releasing noxious materials, nourishing bugs, and wasting resources. Similarly, noxious products from burning can lead to serious environmental pollution. With regard to the reuse of PET waste, recycling is an effective and scientific handling method. Nevertheless, recycling is limited in practice by its high cost. In addition, PET wastes adapted to recycling are limited. For example, wastes, which contain hard to remove additives or impurities, are difficult to recycle. A great deal of PET wastes (e.g., textiles, rubbishes, and films) are not collected and recycled due to the high cost and/or low value[5].

With the development of biological techniques in the 21st century, biodegradation of PET has been proposed as a subject of great potential. Different from chemical degradation; biodegradation has the potential to avoid secondary pollution, while lowering the handling cost. Biodegradation is the best way to address PET and other polymer wastes from the source.

Many scholars and institutes are engaged in the study of biodegradation of PET[6–8] and diethylene glycol terephthalate (DTP). But there are few reports on the biodegradation of PET in which significant direct microbial or enzymatic attack on PET could be observed up to now because of its compact structure. Thus, the study of biodegradation of PET is still in the primary stage.

Because the chemical structure of DTP is similar to that of PET, DTP is one of the best simulating materials for studying the biodegradation of PET fiber. The biodegradability of PET fiber could be discussed through the biodegradation rule of DTP. On the other hand, as a chemical engineering raw material, DTP is an environmental pollutant too. Consequently, the study of DTP biodegradation is important not only for solving its environmental pollution, but also for developing a foundation for the biodegradability study of PET.

Correspondence to: J. Zhang (zhangjianfei@tjpu.edu.cn).

**TABLE I**
**The Composition of Culture Medium**

| Culture medium 1 (M1) | | Culture medium 2 (M2) | |
|---|---|---|---|
| Reagent | Concentration (g/L) | Reagent | Concentration (g/L) |
| DTP | 0.5, 1.0 | DTP | 0.5, 1.0 |
| $NH_4NO_3$ | 0.5 | $(NH_4)_2SO_4$ | 0.5 |
| $KH_2PO_4$ | 0.1 | $KH_2PO_4$ | 0.1 |
| $MgSO_4 \cdot 7H_2O$ | 0.05 | $MgSO_4 \cdot 7H_2O$ | 0.05 |
| NaCl | 0.05 | NaCl | 0.01 |
| Yeast extract | 0.02 | Yeast extract | 0.02 |
| | | $CaCl_2 \cdot H_2O$ | 0.01 |
| pH | 9.0 | pH | 6.0 |

## EXPERIMENTAL

### Experimental Instrument

The following instruments were used: an HZQ-C air bath oscillator (Factory of Dongming Medical Instrument of Haerbin, P.R.China); a LRH-150B incubator (Factory of Medical Instrument of Guangdong Province, P.R.China); KYKY2800 scanning electron microscopy (Factory of Medical Instrument of the Chinese Academy of Sciences) (test conditions: 15 kV, 100 $\mu$m); and a Waters 600E high performance liquid chromatography instrument (HPLC) (test conditions: detector: 996 PDA; chromatogram column: Xterra $RP_{18}$ 5 $\mu$m 150 $\times$ 3.9 mm; wavelength: 240 nm; fluid phase: methanol:$H_2O$ [$KH_2PO_4$ 0.05 $M$/L $H_3PO_4$ $PH_2$] 60:40; flow rate: 1 mL/min).

### Chemicals

The chemicals used were E-3019 lipase (41 units/mg solid, Sigma Co.Ltd.); terephthalate acid (TA): chemical grade; DTP: chromatographic pure; and undrawn PET fiber (amorphism) (Tianjin Petrochemical Co. Ltd).

### Microbial Sources

Four sources of activated sludge were collected at different locations in China: Tianjin Petrochemical Co. Ltd. (T), Zhejiang Yinqiao Chemical Fiber Co. Ltd. (Y), Shaoxing Dyeing and Finishing Co. Ltd. (J), and Fujian Chemical Fiber Co. Ltd. (F).

### Culture Medium and Culture Condition

The microbes were grown in two types of culture medium (Table I). One milliliter of activated sludge was initially suspended in 5 mL of physical saline.

**TABLE II**
**Composition of Degradation Medium 3 (M3)**

| Reagent | Concentration (g/L) | Reagent | Concentration ($\mu$g/L) |
|---|---|---|---|
| Glucose | 2.0 | $H_3BO_3$ | 0.5 |
| $NH_4Cl$ | 1.0 | $CuSO_4 \cdot 5H_2O$ | 40.0 |
| $KH_2PO_4$ | 3.0 | $FeCl_3 \cdot 6H_2O$ | 0.2 |
| $MgSO_4 \cdot 7H_2O$ | 0.25 | $ZnCl_2$ | 0.4 |
| $Na_2HPO_4$ | 7.0 | $MnSO_4 \cdot 5H_2O$ | 0.4 |
| NaCl | 0.5 | $(NH_4)_6Mo_7O_{24} \cdot 7H_2O$ | 0.2 |
| DTP or PET (substrate) | 5.0 | pH | 6.8 |

**TABLE III**
**Analysis of DTP Degradation Solution by Microbe Using HPLC**

| Order | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Culture medium | M2 | M1 | M1 | M1 | M1 |
| Culture pH | 6 | 9 | 9 | 9 | 9 |
| Microbe source | T | T | Y | J | F |
| DTP (g/L) | 5 | 5 | 5 | 5 | 5 |
| Degradation condition | M3; 14d | M3; 14d | M3; 14d | M3; 14d | M3; 14d |
| Residual TA content | | | | | |
| (mg/L) | 1.74 | 0.89 | 1.42 | 0.28 | 3.00 |
| (%) | 0.58 | 0.29 | 0.48 | 0.09 | 1.00 |
| Residual DTP content | | | | | |
| (mg/L) | 209.89 | 11.30 | 26.56 | 5.87 | 32.00 |
| (%) | 52.54 | 2.83 | 6.64 | 1.47 | 8.00 |
| Degradation ratio | | | | | |
| (%) | 47.5 | 97.2 | 93.4 | 98.5 | 92.0 |

**TABLE IV**
**Effect of Microbe Degradation Time on DTP Degradation Ratio**[a]

| Degradation time (day) | Original DTP content (g/L) | Residual DTP content (g/L) | Degradation ratio (%) |
|---|---|---|---|
| 1 | 5.000 | 4.410 | 11.8 |
| 2 | 5.000 | 0.816 | 80.8 |
| 4 | 5.000 | 0.340 | 93.2 |
| 6 | 5.000 | 0.252 | 95.0 |
| 8 | 5.000 | 0.135 | 97.3 |
| 10 | 5.000 | 0.035 | 99.3 |
| 14 | 5.000 | 0.045 | 99.1 |

[a] Culture medium, M1; pH = 9, microbe source, T; degradation medium, M3; test method, HPLC.

Then about 1 mL of suspension was added to 50 mL of culture medium M1 or M2 and incubated for 7 days at 30°C. Experiments were conducted in triplicate. Microbes screened were considered a model microbes source for degradation of PET fiber or DTP.

### Degradation Medium and Degradation Method

PET was degraded in medium 3 (Table II). A total of 0.2 mL of microbe solution was transferred from culture M1 or M2 to 2 mL of degradation M3. Then M3 was incubated at 30°C for 14 days. After that, 4.67 mL of methanol was introduced to the degradation solution (M3) to dissolve residual substrate, which made the final concentration of methanol 70%. Subsequently, the solution volume was brought to 25mL using 70% methanol prior to measurements.

## RESULTS AND DISCUSSION

### Influence on Degradation Ratio of DTP by Different Microbes

DTP was degraded with microbes screened under fixed conditions. The biodegradation ratio was determined by HPLC. Results are given in Table III.

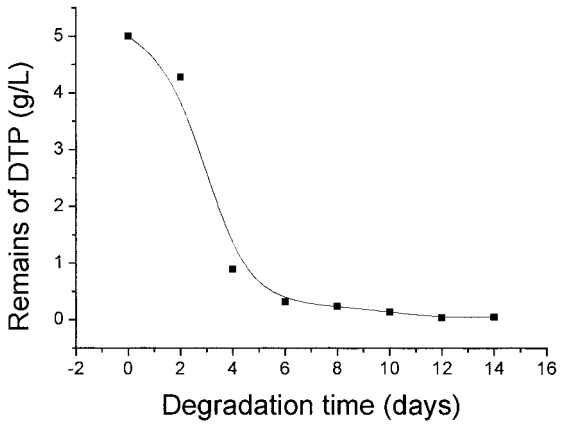



**Figure 1** Variation of residual DTP content in degradation solution with time.

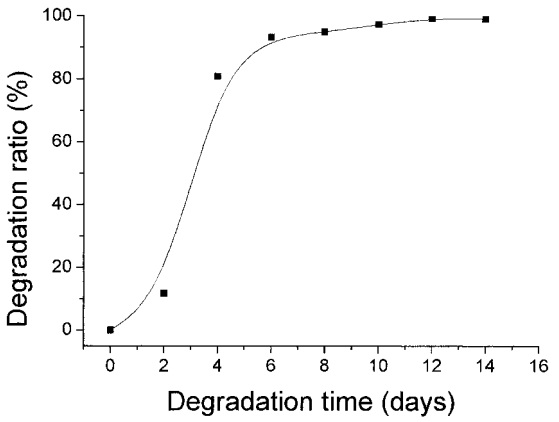



**Figure 2** Relations of DTP degradation ratio with time.

As demonstrated in Table III, the amount of TA produced was very small because TA was only a primary intermediate of DTP, which could be decomposed further to lower molecular products by microbes. Therefore, the precise determination of residual TA in degradation solution could not correctly reflect the degradation ratio of DTP. In contrast, it could be calculated by residual DTP content in the degradation solution.

Apart from the microbe incubated in culture M2, other strains screened showed high degradation activity for DTP and the degradation ratios were all above 92%, indicating that microbes, which had high degradation activity for DTP, existed in nature. If the biodegradation technology is optimized, it is possible to degrade DTP completely. Owing to the biodegradation complexity, the particular products of DTP degraded by microbes were not clear and the degradation mechanism needs further study.

### Effect of Microbe Degradation Time of DTP on the Degradation Ratio

Microbe T screened was selected for further study to determine the influence of reaction time of DTP deg-

**TABLE V**
**Variation of Lipase Degradation Ratio of DTP, Peak Area with Time**[a]

| Time (h) | Original DTP (mg) | Residual DTP (mg) | TA peak area (%) | Peak 4 area (%) |
|---|---|---|---|---|
| 1 | 50 | 35.26 | 0.29 | 10.82 |
| 2 | 50 | 33.83 | 0.76 | 12.89 |
| 4 | 50 | 34.37 | 2.47 | 6.98 |
| 10 | 50 | 32.99 | 12.75 | 2.51 |
| 24 | 50 | 28.83 | 12.69 | 0.98 |

[a] buffer solution, trihydroxy methylaminomethane–HCl; pH = 8; $T$ = 30°C; lipase content: 1.5 unit/mg substrate; test method, HPLC.

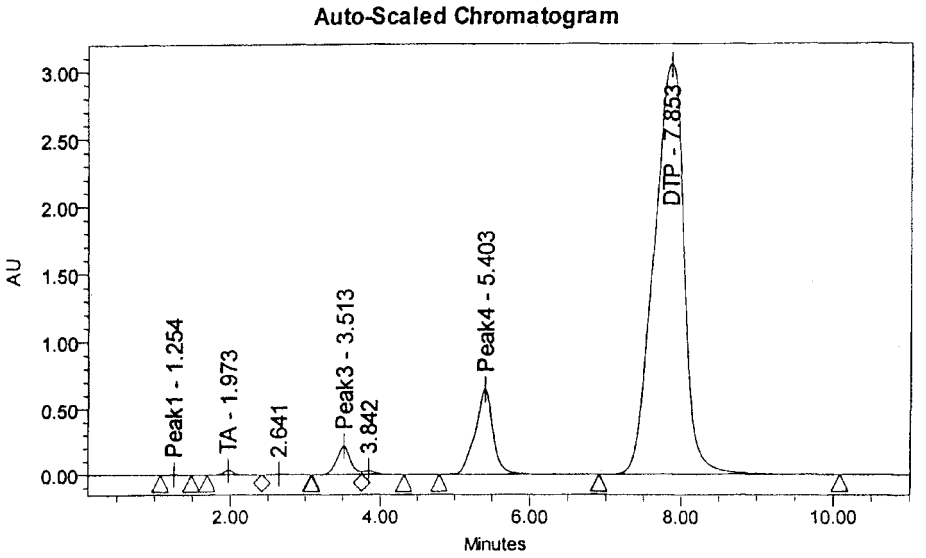



**Figure 3** HPLC diagram of degradation solution degraded for 1 h.

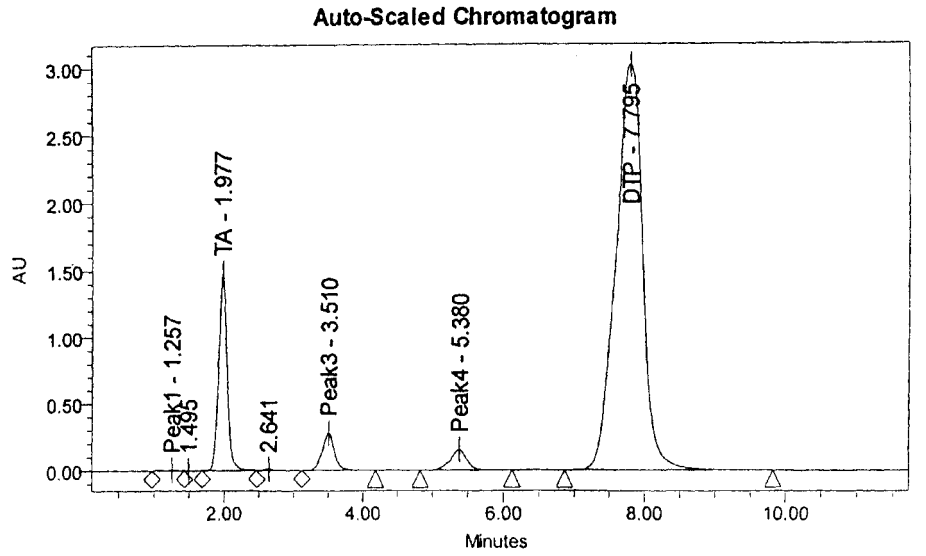



**Figure 4** HPLC Diagram of degradation solution degraded for 10 h.

radation. Experimental conditions and results listed in Table IV and Figures 1 and 2.

As presented in Table IV and Figures 1 and 2, the degradation ratio reached more than 90% after 4 days of degradation. The microbial degradation rate of DTP was consistent with the characteristic first-order reaction model and could be expressed with the equation

$$\ln S = -kt + \ln S_0,$$

where $S_0$ and $S$ denote the original concentration and instantaneous concentration of DTP, respectively; $k$ is the rate constant; and $t$ is the reaction time. Thus, in our study, the kinetic equation of DTP was

$$\ln S = 1.3766 - 0.4733t,$$

where $k = 0.4733(\mathrm{d}^{-1})$; half-time $t_{1/2} = (\ln 2)/k = 1.465(\mathrm{d})$; and correlation coefficient $r = 0.9691$.

### Effect of Lipase Degradation Time for DTP Degradation

Lipase showed some degradation ability for DTP as well. Experimental conditions and results are given in Table V and Figures 3 and 4.

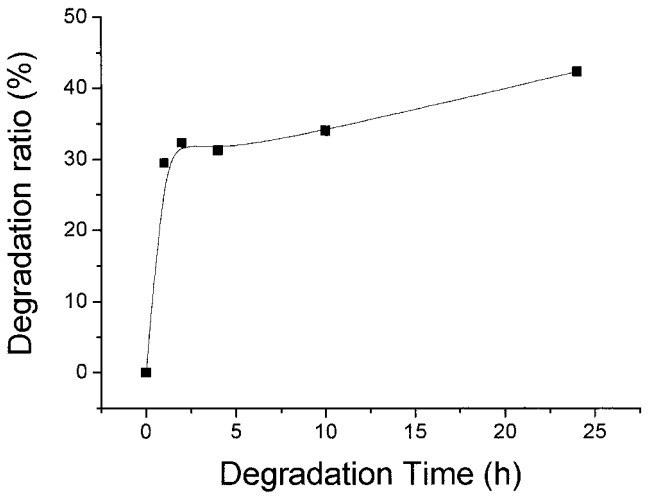



**Figure 5** Change of degradation ratio of DTP degraded by lipase with time.

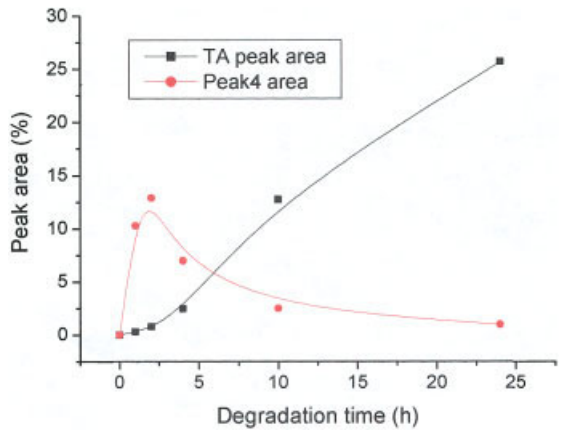
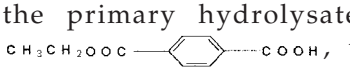
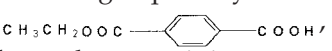



**Figure 6** Change of TA and peak 4 area in the degradation process.

Along with degradation time extension, the HPLC chromatogram diagrams were similar, so two typical chromatogram diagrams were selected. The difference between the chromatogram diagrams was that the peak height and peak area of the TA peak and peak 4 varied, and their change rules are shown in Table V and Figures 5 and 6.

As shown in Table V and Figures 5 and 6, the degradation ratio increased very quickly at the beginning and then gradually decreased afterward. The degradation ratio arrives at 42.33% after 24 h of reaction. The change rule of TA peak area and peak 4 area, which varied with reaction time, is explained in Figure 5. From the change of the TA peak area and peak 4 area, it could be deduced that lipase did not transform DTP to TA directly; instead, the primary hydrolysate of DTP might be  , the retention time of which should be 5.4 min on the HPLC diagram. It was found that the peak 4 area increased initially and then decreased gradually with continued reaction, accompanied by a TA peak area gradual increase. Accordingly, the following conclusion could be drawn. After lipase attack at the ester bond of a DTP molecule, lipase did not continue to hydrolyze the other ester bond of the same DTP molecule at once; instead, it attacked the ester bond of other DTP molecule. After accumulating a quantity of the primary hydrolysate  lipase started to hydrolyze the remaining ester bonds of the intermediate to form TA. The reaction equation of DTP degraded by lipase followed the expression

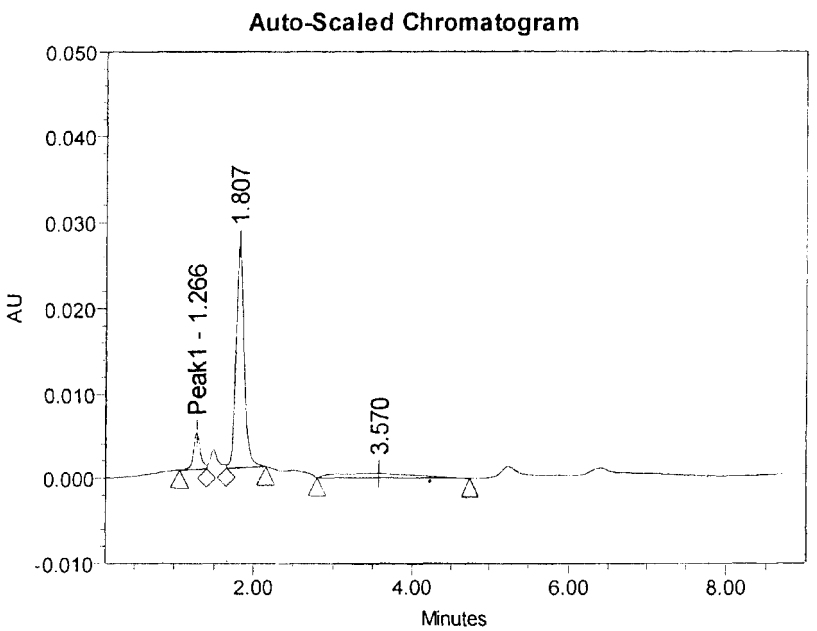



**Figure 7** HPLC diagram of treated PET fiber degraded by lipase.

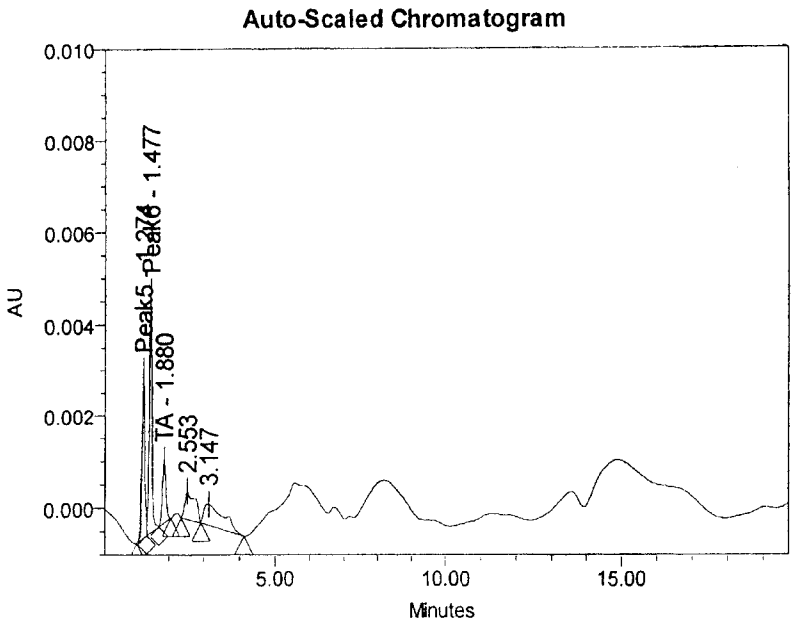
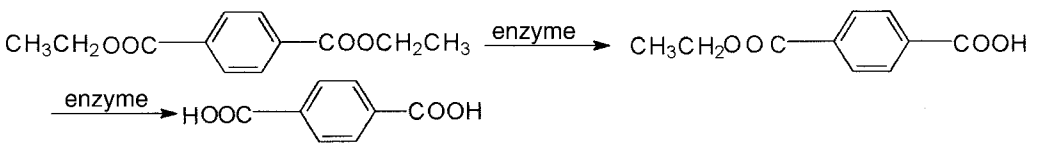



**Figure 8** HPLC fiagram of treated PET fiber degraded by microbe.




**Biodegradation of PET Fiber**

Even if microbes and lipase showed excellent degradation activity with DTP, the degradation of PET fiber by these microbes and lipase was very weak, and is not considered practical for industrial use in reducing PET pollution. But there was evidence of degradation from HPLC diagrams (Figures 7 and 8) and SEM micrographs (Figures 9–11) of treated PET fiber.

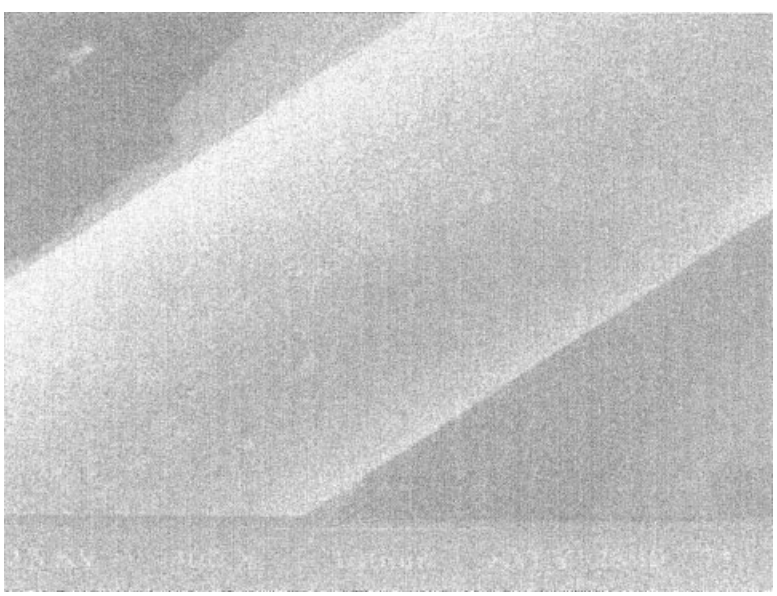


**Figure 9** SEM micrograph of untreated PET fiber surface (original magnification 300×).

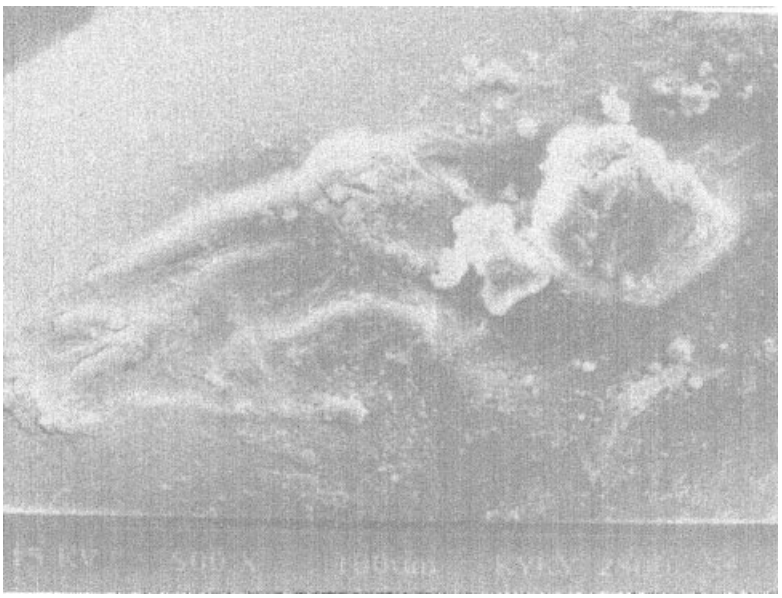


**Figure 10** SEM micrograph of PET fiber surface treated by microbe (original magnification 800×).

As shown in the HPLC diagrams, there was minimal TA in the degradation solution, after a retention time of about 2 min, because the degradation of PET produced TA. SEM micrographs of PET fiber treated by microbe or lipase (Figures 10 and Fig. 11) showed obvious signs of fiber surface erosion. Correspondingly, cracks and voids were not observed in untreated PET fiber surfaces, demonstrating that microbe and lipase could act on PET and cause weak degradation. But, because the structure of PET was very compact and the fiber surface was too smooth, it was difficult for the microbe or lipase to attach and degrade, and the erosion signs are shallow, few, and far between.

## CONCLUSION

1. Microbes screened showed significant degradation of DTP and the degradation ratio could amount to over 90%. Therefore, they could help solve the problem of environmental pollution caused by DTP. The degradation activity of lipase was observably weaker

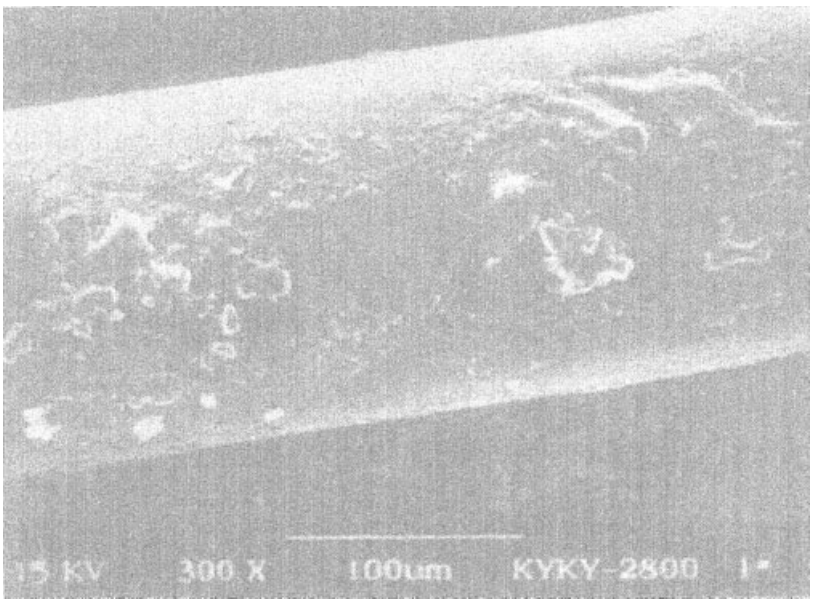
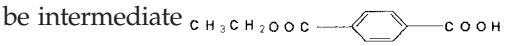



**Figure 11** SEM micrograph of PET fiber surface treated by lipase (original magnification 300×).

than that of microbes, and the degradation ratio of DTP degraded by lipase only reached 40%. Further studies on screening lipase and degradation technology could be carried out.

2. The degradation of DTP by microbes followed the first-order kinetic equation and the degradation ratio reached over 90% after 4 days of reaction.

3. During the process of DTP degradation by lipase, there might be intermediate  which transformed to TA ultimately after 24 h of reaction.

4. Although degradation of PET fiber by microbes or lipase was very weak, from SEM micrographs and HPLC analysis it was shown that microbe and lipase can act on PET and cause some degradation.

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