# Polyester Recycling

Project 5: Reuse, recycling and end of life issues

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Within project 5, two recycling methods, physical recycling and chemical recycling, have been tested to recycle polymeric textile waste. In physical recycling, polymeric fiber waste were compounded and then re-spun into fiber by a melt spinning process. In chemical recycling, the polymeric fiber waste (polyester fiber waste) was chemically depolymerized into its monomers, and then the generated monomers were collected and purified. The purified monomers are suitable for virgin polymer synthesis.

1. Physical recycling

In this recycling study, two kinds of post-consumer polymeric fibers were tested. The samples are shown in figure 1. They are polypropylene (PP) nonwoven fabric and Polyester (mainly polyethylene terephthalate (PET)) staple fibers provided by SOEX in Germany.
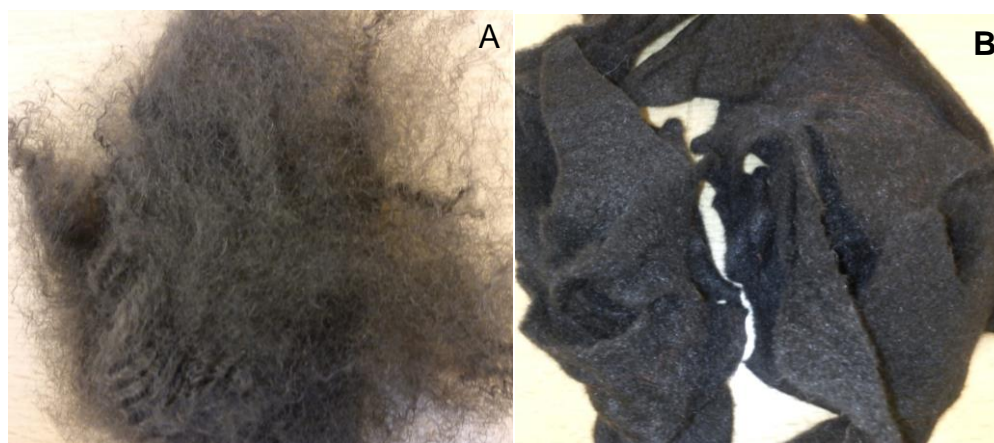
Figure 1 Two different kinds of post-consumer polymeric fibers for recycling: A: PET staple fibers; B: PP non- woven fabric.

1.1 Experimental part

DSC measurements

DSC measurements were performed on a DSC1 instrument from Mettler Toledo under the nitrogen atmosphere. Around 5 mg of sample was sealed in an aluminum pan for DSC measurements. Two heating and one cooling scans between 30 °C and 280 °C were performed. The heating and cooling rates were 10 °C/min and 5 °C/min, respectively.

FTIR measurements

FTIR measurements were carried out by using a Perkin Elmer instrument with a Specac Golden Gate attenuated Total Reflectance (ATR). The resolution of spectrometer is 4 cm^{-1} and the spectra are recorded with an accumulation of 6 scans.

Chemical hydrolysis

The hydrolysis of PET in the post-consumer PP sample was performed in 1 M NaOH solution. Around 35 g of recycled PP fabric was cut into small pieces and then put in 500 ml NaOH solution at around 80 °C. The solution was stirred for overnight. After hydrolysis, the PP fabric was washed by excess water and dried at 75 °C for overnight.

Xylene extraction

1g PP fabric was cut into small pieces and put into xylene at around 110 °C. The xylene solution was stirred for 5h, and then the fabric was taken out from the xylene and washed by excess acetone. The washed fabric was put in a vacuum oven at 60 °C and dried for overnight.

Compounding and Melt-spinning of recycled PP and PET

The recycled PP fabric was compounded in brabender kneader. The compounding temperature was 240 °C and compounding time was 5 min. The screw rotation speed was 100 rpm. The compounded PP sample was then pelletized for the melt-spinning test.

The spinnablity of post-consumer polymers was tested in a capillary rheometer as showed in figure 2. The piston speed was 20 mm/min. The capillary is 10 mm in length and 1 mm in diameter. For the PP sample, the melt-spinning temperature was 240 °C, and for PET sample, the melt-spinning temperature was set to 280 °C.
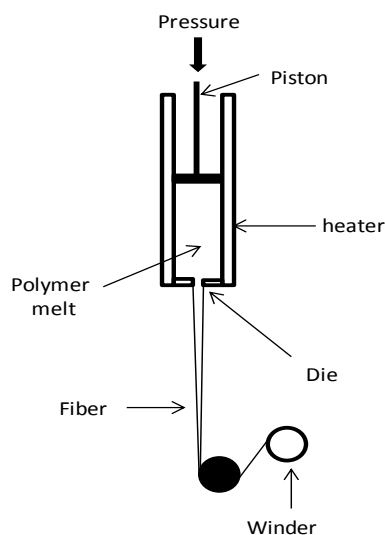
Figure 2 The scheme of fiber spinning process by using capillary rheometer.

1.2 Results and discussion

Analysis of the composition of recycled polymer

The composition of post-consumer PP and PET samples was analyzed by DSC. As shown in figure 3a, there is only one DSC peak in heating and cooling scans of PET, which is ascribed to the crystal structure of the PET. The presence of one peak in DSC scans of the PET sample indicates that the PET has a very high purity. However, for the PP sample, two DSC peaks could be clearly observed in heating and cooling scans (figure 3b). The peak at low temperature is due to the presence of crystal structure in PP, while the peak at high temperature is probably ascribed to the presence of PET. The presence of PET in the PP sample is also confirmed by FTIR measurements. In figure 4, it can be seen that the FTIR spectrum of recycled PP fabric is quite similar as the spectrum of PET, especially the peak at 1712 cm^{-1} indicating the presence of ester bond in PP fabric sample. In addition, the cluster peaks at around 2800 cm^{-1} prove the presence of PP in the post-consumer PP fabric. So, based on the DSC and FTIR analysis, the post-consumer PP fabric is not pure PP, but contains another component of PET.
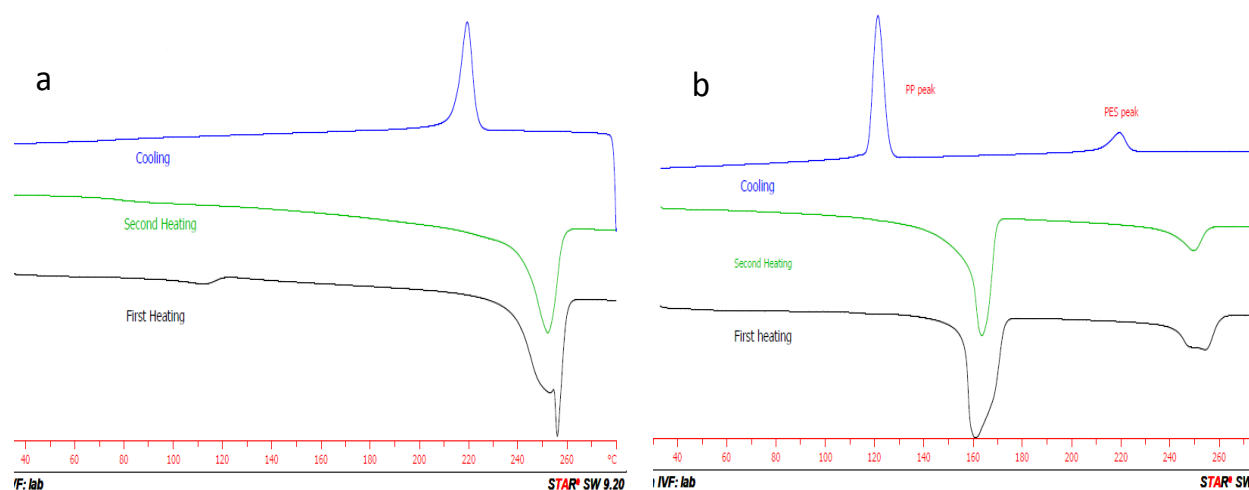
Figure 3 DSC analysis of recycled PET sample (a) and Recycled PP sample (b).

The amount of PET in the PP sample was also analyzed by hydrolyzation of PET. In the hydrolysis method, the PET concentration is calculated to be around 16.6 wt%. Based on the literature, it is impossible to completely hydrolyze the PET even in a highly concentrated NaOH solution. So, the PET impurity concentration in the PP sample is probably higher. In order to know the accurate concentration of PET in the PP sample, another method which is the extraction of PP by hot xylene was tried. In this method, the concentration of PET impurity in the PP sample turned out to be around 29.57 wt%. According to literature, PP has a good solubility in hot xylene. The PP in the PP sample should be completely dissolved in hot xylene. So the PET impurity concentration calculated by this method is probably more accurate. It means that there is only around 70 wt% of PP in the "so-called" post-consumer PP sample.
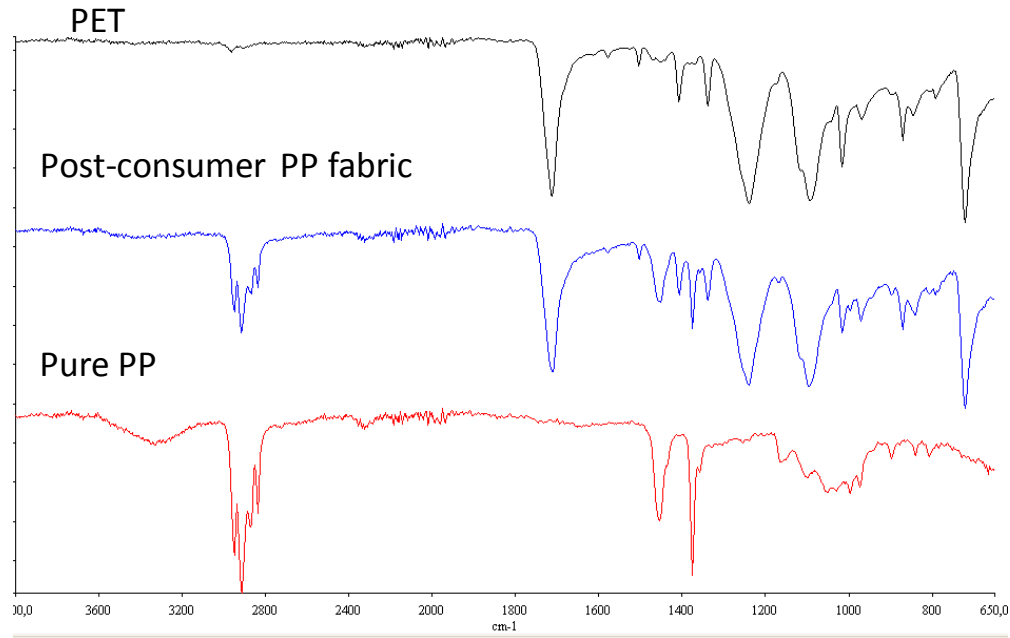
Figure 4 FTIR spectra of PET, post-consumer PP fabric and pure PP.

Compounding and melt-spinning recycled PET and PP sample

Post-consumer PET stable fiber

Since post-consumer PET sample has a high purity, it is very easy to compound and then re-spin the PET sample into fiber.

Post-consumer PP fabric

After compounding the sample at 240 °C for 5 min, a lot of un-melt fibers are still found in the PP matrix as shown in figure 5. The presence of such impurity fibers makes the melt-spinning of recycled PP fabric impossible. The intact fiber in compounded PP matrix is probably PET fibers since the PET have a very high melt temperature (above 250 °C). To reduce the negative influence caused by the presence of PET fiber on the melt spinning of post-consumer PP fabric, the recycled PP fabric was hydrolyzed in NaOH solution. The hydrolyzed PP fabric was compounded under the same conditions as before. No fiber could be observed in the PP matrix, even there is still a small amount of unhydrolyzed PET in the PP as shown in DSC analysis in figure 7. In the melt spinning test, the hydrolyzed PP sample still shows a very poor spinnability. Only short filaments could be produced and these short filaments are very brittle. Sometimes, the polymer melt was even dripping as indicted in figure 6. This probably indicates that some part

of PP is severally degraded. Generally, the presence of PET and degradation of PP lead to recycled PP as unspinnable.
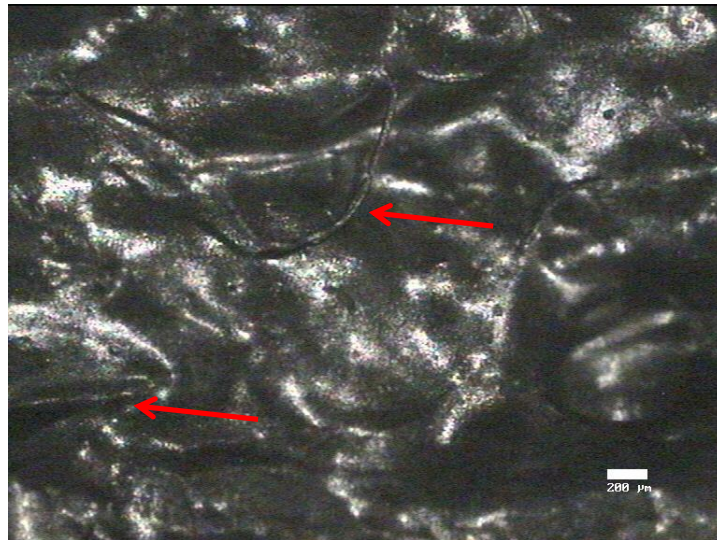
Figure 5 Optical image of compounded PP sample. The red arrows indicate the presence of intact fiber.

Figure 6 Image of short fiber prepared by melt spinning of hydrolyzed PP sample. The red arrows indicate the PP polymer melt dripped during spinning process.
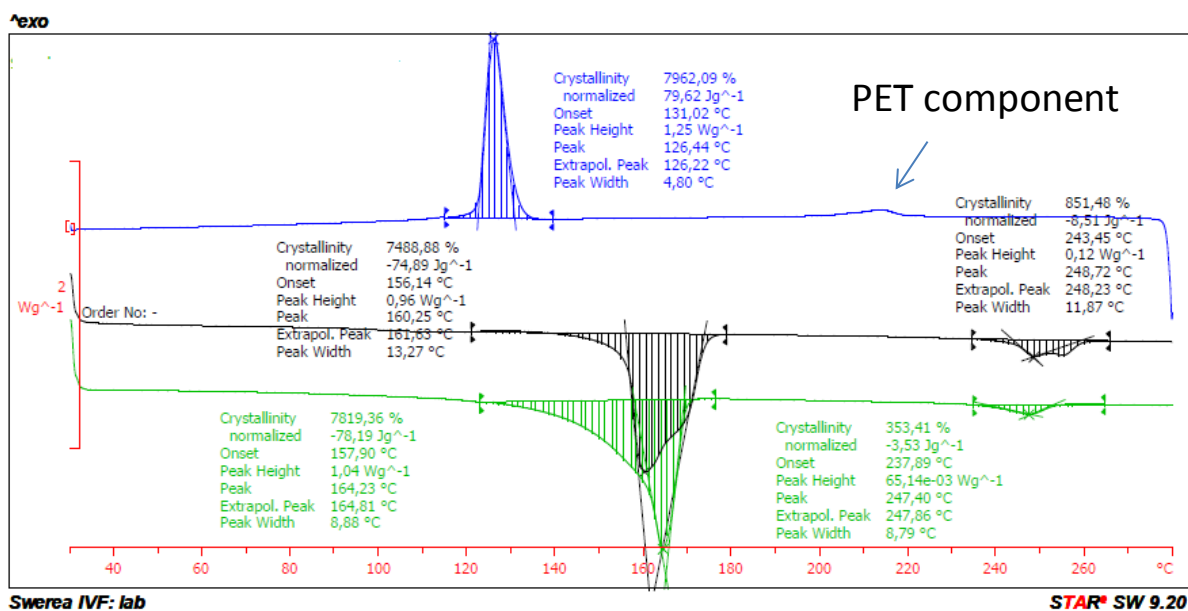
**Figure 7** DSC scans of recycled PP fabric after hydrolysis.

2. Chemical recycling

For polyester fiber waste from cloth, it is found that the polyester has already degraded into low molecular weight polymer as revealed by a significantly decrease of viscosity as shown in figure 8. In addition, the composition of textile waste is complicate. Different polymeric fibers or natural fibers may coexist in the polyester textile waste, for example polyester/cotton (50: 50) blended textile. Therefore, the physical recycling (melt spinning) is no longer suitable. To recycle this kind of polyester textile waste, chemical recycling is necessary. In this study, glycolysis of post consumer polyester fabric (polyethylene terephthalate, PET) provided by SOEX is investigated (scheme 1). In addition, the virgin PET was also glycolysized as the reference.
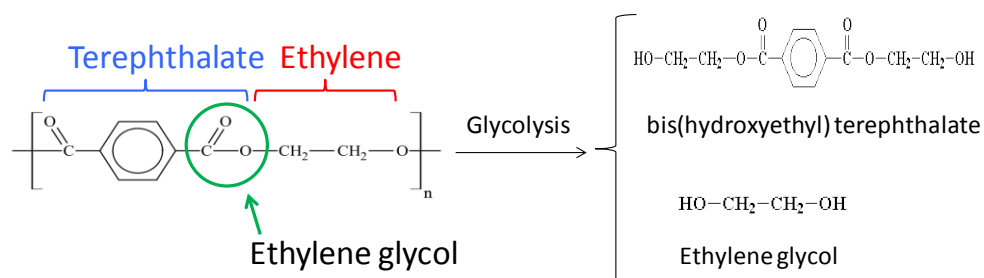
Scheme 1. Glycolysis of polyester (polyethylene terephthalate, PET)
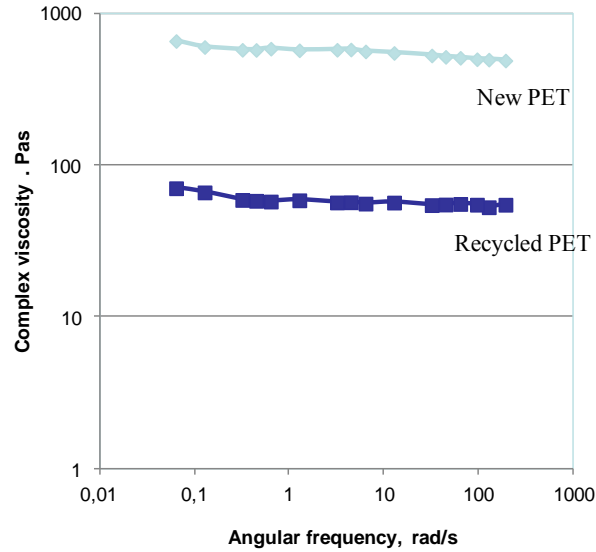
Figure 8 Viscosity of new PET and post-consumer PET. The measurements were performed at 270°C under nitrogen atmosphere.

2.1 Experimental part

Glycolysis of PET

5 g PET and 30 ml glycol were added into autoclave. Before sealing the autoclave, it was purged with pure nitrogen gas to remove air to avoid possible oxidation of PET under glycolysis. The prepared autoclave was heated up to a desired temperature in an oven. After a certain time, the autoclave was taken out from the oven and put into cold water to quench the reaction. To quantitively determine the depolymerization efficiency and yield of monomer bis(hydroxyethyl) terephthalate (BHET), the reaction system was washed several times with 150 ml boiling water (deionized water). The obtained suspension was quickly filtrated to collect undepolymerized PET. The undeplymerized PET was dried in an oven at 100°C over night and weighted and labeled as w_1. The filtrate obtained from the first filtration was filtrated again to remove BHET dimer which only dissolves in water at high temperature and precipitates at room temperature in water. The collected filtrate was cooled to 4°C over night to crystallize BHET. To further purify the BHET, crystallization and filtration of BHET were repeated for two times. The final weight of BHET obtained was labeled as w_2. Therefore, the depolymerization efficiency of PET can be calculated by Eq. 1 and yield of BHET can be defined by Eq. 2.

$$\text{Depolymerization efficiency \%} = \frac{w_0 - w_1}{w_0} \text{ X } 100\% \qquad \text{Eq. 1}$$

$$\text{Yield of BHET (mol \%) } = \frac{\textit{Moles of BHET produced}}{\textit{Moles of PET units}} \text{ X100\%} \qquad \text{Eq. 2}$$

Where w_0 is the weight of PET before depolymerization.

Addition of nanocatalyst

The addition of nanocatalyst into the depolymerization system was made by the compounding of nanocatalyst with PET. PET and nanocatalyst was dried at 110°C overnight before compounding. 40g of PET and certain amount of nanocatalyst were compounded in a brabender kneader at 270°C for 5min. After compounding, PET/nanocatalyst composites were pelletized and grinded into fine powder.

Results and discussion

Studying the nanocatalyst

In order to improve the depolymerization efficiency, different kinds of trans-esterifaction catalysts have been studied as catalyst to glycolysize the PET according to the literature. Among them, zinc acetate is reported to be the most efficient catalyst in the glycolysis of PET. However, as the zinc ion cannot be degraded in nature and is harm for the environment, it is necessary to investigate other catalysts as the trans-esterifcation catalyst in glycolysis of PET. In our work, we found that the synthetic nanocatalyst was very efficient to catalyze the glycolysis of PET. Different from catalyst containing zinc ion, this nanocatalyst is environmentally benign and can be directly disposed into environment without cause any environmental pollution.

To study the catalyst efficiency, we used virgin PET as reference. As shown in figure 9, the deploymerization efficiency of PET at 240°C in the absence of nanocatalyst is just above 40% and no BHET monomer is recovered at this conditions. However, when there is only 0.1 wt% of nanocatalyst in the reaction system, the depolymerization efficiency increase to more than 80% and the yield of BHET is around 70%. As the nanocatalyst concentration increase, the depolymerization efficiency and yield of BHET are also increase and reach to the maximum value at the nanocatalyst concentration of 0.5 wt%.
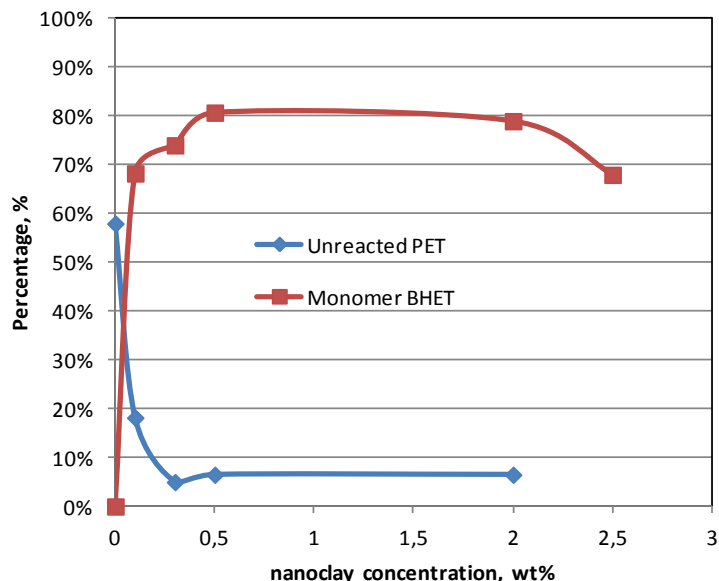
Figure 9 Depolymerization of PET by glycolysis. The reaction temperature was 240°C and reaction time was 1 h.

The presence of nanocatalyst can also reduce the reaction temperature. When the reaction temperature decreases from 240°C to 200°C, there is no reaction in the PET system without nanocatalyst. While, when there is 0.5 wt% of nanocatalyst in the system, the yield of BHET is more than 60% under the same reaction conditions. The lowering the reaction temperature means to save the energy. This is more practical for industrial recycling of PET.

FTIR analysis of obtained BHET

The obtained BHET was analyzed by FTIR. As a comparison, the commercial BHET bought from Sigma-Aldrich with a purity of more than 99% was also recorded a FTIR spectrum. The FTIR spectra of obtained BHET and commercial BHET are listed in figure 10. Obviously, the FTIR spectrum of BHET obtained from depolymerization is identical to that of commercial BHET with a high purity. This indicates that the obtained BHET from depolymerization is a BHET with a high purity.
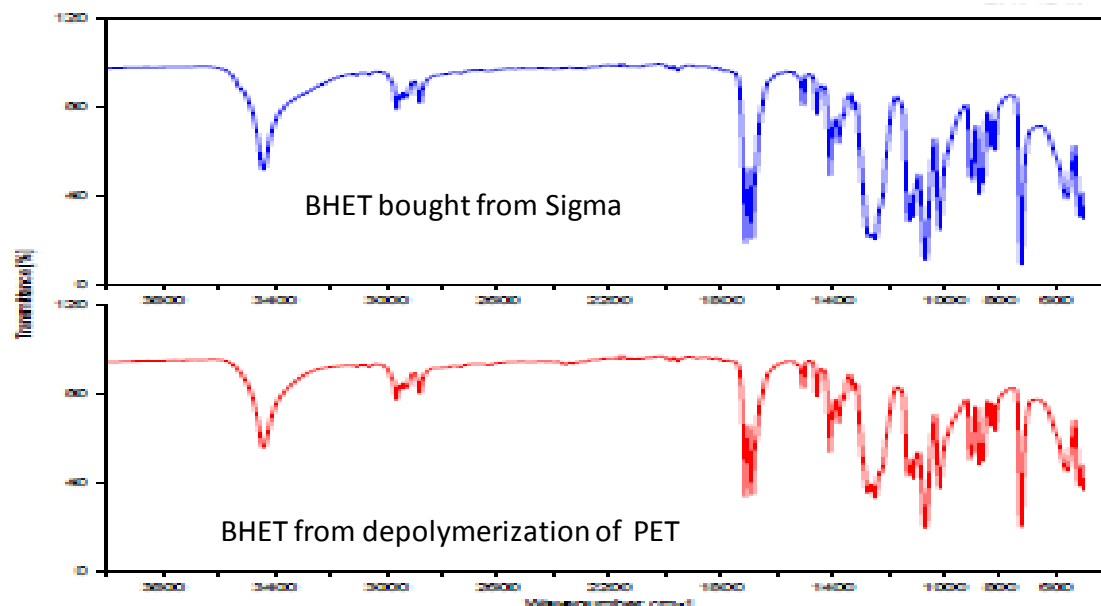
Figure 10 FTIR spectra of BHET

Compounding PET textile waste with nanocatalyst

PET textile wastes were compounded with different amounts of nanocatalyst in a small brabender kneader at 270°C for 5min. After compounding, the PET with different amounts of nanocatalyst was analyzed by DSC to check their degradation level. As shown in figure 11, the melting point of PET after compounding with nanocatalyst decreased compared to PET without addition of nanocatalyst, which indicates that the PET has started to degrade during the compounding process. As the nanocatalyst concentration increase, the degradation of PET becomes more obvious. When there are 10 wt% of nonaclay in the PET, the PET shows a broad melting peak and melting temperature decreases to 250°C after compounding. The presence of broad and low melting peak indicates the PET has experienced a significant degradation and the degraded PET has broad molecular weight distribution.
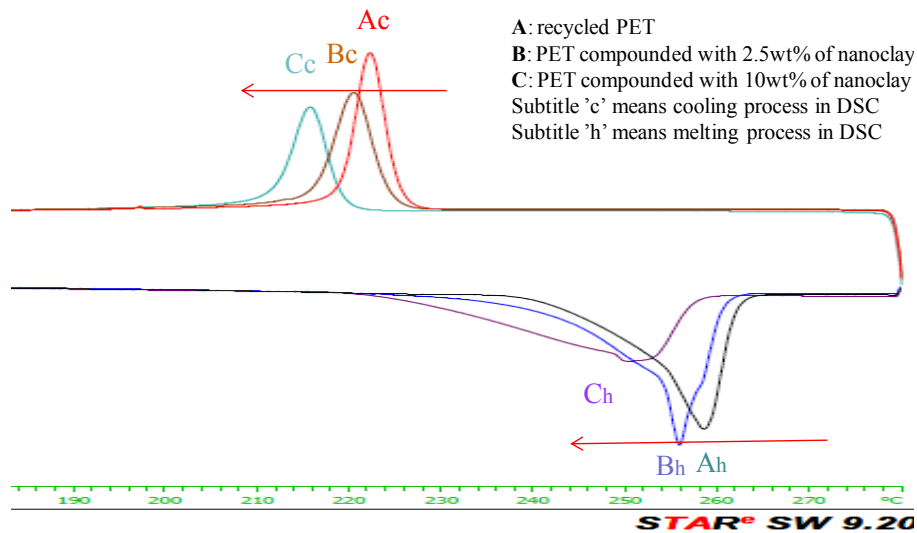
Figure 11 DSC curves of PET before and after compounding with nanocatalyst

3. Conclusion

Physical recycling

1. The received PET staple fibers waste has high purity and can be re-spun into fiber.
2. The received PP fabric waste contains around 30 wt% of impurity which are probably PET. The spinnability of this PP sample is very poor even the impurity of PET is partially removed by hydrolysis in NaOH solution.

Chemical recycling

1. Polyester from cloth waste has been degraded and it is not suitable for physical recycling process (melt spinning).
2. Synthetic nanocatalyst works as efficient catalyst in glycolysis of PET.

4. Future works

1. Optimization of the glycolysis of PET in the presence of nanocatalyst.
2. Reactive glycolysis of PET during compounding with nanocatalyst is very interesting to test. During the compounding step, the PET can react with glycol and degrade into low molecular PET or even oligomer. Therefore, low reaction temperature and short reaction time is needed for the following glycolysis step in autoclave.

3. Purification of BHET from different pigments. The textile wastes have different colors. After glycolysis, the pigment molecules mix with BHET and some of them could co-crystallize with BEHT into crystal. An easy and practical way of purification of BEHT is necessary for glycolysis of PET in textile waste. The following figure shows the different color of BEHT recovered from glycolysis of virgin PET and PET textile waste.
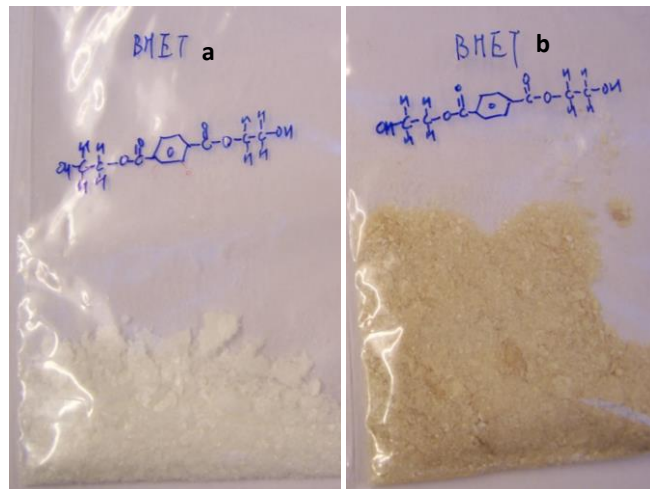

Figure 12 BEHT recovered from the glycolysis of PET process. a: PET is virgin PET; b: PET is PET textile waste with different colors.