Separation and recycling of cotton from cotton / PET blends by depolymerization of PET catalyzed by bases and ionic liquids

J. Oelerich, R. A. J. Groeneveld, G. H. Bouwhuis and G. J. Brinks

Saxion University of Applied Sciences
Research Centre Design and Technology, The Netherlands
j.j.oelerich@saxion.nl

Abstract: The recycling of post consumer cotton textile waste is highly requested, due to the high environmental impact of cotton production. Often cotton is mixed in blends with polyethylene terephthalate (PET). For the generation of high value products from recycled cotton, it essential that PET is separated from the cotton first. In this contribution, the depolymerization of PET in cotton / PET blend is investigated for the separation of PET from cotton fibers. Ionic liquids and NaOH are used as catalysts for the depolymerization reaction in ethylene glycol (glycolysis). It will be shown that ionic liquids have no significant influence on the conversion of PET. However, 99% conversion is achieved in this process with 2 w/w % NaOH as catalyst. This enables the selective depolymerization of PET in presence of cotton and gives rise to an easy separation of cotton from cotton / PET blends.

Key Words: SaXcell, cotton recycling, PET depolymerization, ionic liquids

1. Introduction

Despite our high standards in technology worldwide most of the textile waste is burned at the end of its life cycle. Considering the enormous need of water and fertilizers used for growing the cotton plant, this creates a high environmental burden. The demand of cotton will most likely grow with the growth of world population, while at the same time suitable land for cotton cultivation will decrease due to the higher demand on food and biofuels [1]. For that reason, recycling of cotton textile waste by creation of a closed material cycle is a highly prestigious goal for research in applied science.

1.1 SaXcell

In our research group, we investigate methods to recover and recycle cotton. Recently, we developed SaXcell™, a regenerated cellulosic fiber made out of pure uncolored cotton waste material (Picture 1).

A)   B)

Picture 1. A) SaXcell™ logo. B) SaXcell™ production process from fibers to knitted fabric.

1.2 The cotton pretreatment process

Before cotton can be recycled in the SaXcell[TM] process efficiently, all other co-components in cotton blends must be removed. While the recycling of cotton alone is challenging already [2], cotton blends containing dyes, finishes and high mass fractions of polyethylene terephthalate (PET) [3] or other raw materials need additional treatments (Scheme 1).
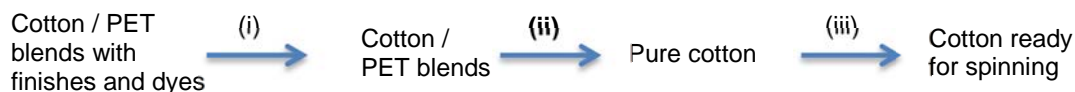

Scheme 1. Pretreatment process for cotton / PET waste material. (i) all dyes and finishes have to be removed from the cotton blend. **(ii) Process step reported in this paper; PET is removed by catalytic depolymerization.** (iii) Pure cotton material needs to be processed further to be ready for spinning.

The process for the pretreatment of textile post consumer waste covers three important steps. The waste has to be unraveled prior to this process. All dyes and finishes have to be removed in a first step to ensure a colorless cotton product after spinning. Spinning of recovered cotton has been optimized for pure cellulose material. For that reason, all other raw material needs to be removed, as well. This step is investigated during the study described in this contribution. When only cellulose containing material is left the cotton will be processed to be ready for spinning.

1.3 Depolymerization of PET

Reversible polycondensation (depolymerization) of PET - that represents the main co-component in cotton blends - can be achieved in several ways. The uncatalyzed depolymerization of PET by water, alcohols or glycols is very slow. This is one reason for the bad degradability of this material in nature. However, several catalysts are known to speed up these reactions to form smaller oligomers or ideally the monomer units. This gives back the raw materials or other useful industrial chemicals to form a closed material cycle [4].

Metals like zinc, magnesium or iron are often used as catalysts for PET depolymerization, but those catalysts could potentially pollute the remaining cotton. For the last step of the pretreatment process (scheme 1) any metal pollution of the cotton has to be avoided. For that reason, metals cannot be used as catalyst, here. Ionic liquids do not contain elements that hamper the recycling process. [Bmim]Br and [Bmim]OH are two well known ionic liquids that can catalyze the depolymerization of PET [5]. Bases like LiOH or NaOH are also known to accelerate the depolymerization process [3].
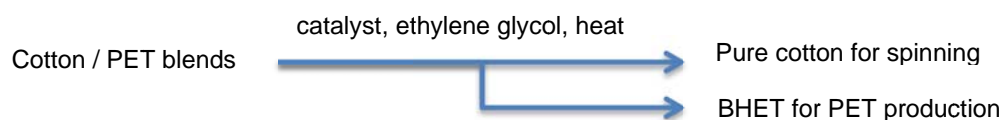
Scheme 2. Selective catalytic depolymerisation of PET.

When an entire depolymerization of PET in ethylene glycol can be achieved, the monomer bis(2-hydroxyethyl)terephthalate (BHET) is formed. This is also the raw material of PET production and could be used again in the production of new PET products (Scheme 2).

2. Materials and Methods

2.1 General remarks

All chemicals were purchased from Fisher Scientific and used without further purifications. The unraveled textile materials were produced by Texperium (The Netherlands).

2.2 Representative procedure for the determination of the cellulose content in blends

The cellulose blend sample was dried for at least 60 min at >100°C. 20 ml 65% solution of sulfuric acid was added into a 100 ml beaker and preheated while stirring to 60°C. 2 g of the sample was weight (W_0) and added to the sulfuric acid solution. The sample was incubated for 3 minute and subsequently filtered over a glass filter. The remaining sample was washed at least 10 times with 20 ml hot distilled water and 5 times with distilled water at room temperate. The residual sample was dried and weight (W_1). The cellulose content in the blend is defined by (W_0-W_1)/W_0 x 100 %. substrate $= \frac{W0-W1}{W0}$ x100%Where W_0 represents the initial weight of the sample and W_1 represents the weight of the remaining sample. The experiments were repeated at least 3 times and the data were averaged.

2.3 Representative procedure for the depolymerization reactions

The pure PET or cotton blend sample was dried for at least 60 min at >100°C. An oil bath was preheated to the indicated temperature. A 50 mL round-bottom flask equipped with a stirring bar (40 x 20 mm, oval) and a reflux condenser was loaded with the catalyst, 1.00 g of dried sample and 20 ml of ethylene glycol (liquor ratio of 1:20). The depolymerization reactions were carried out under atmospheric pressure at the indicated temperature for reaction times of 2 h or 6 h. After the reaction, the remaining sample was quickly separated from the hot liquid phase by filtration. Then 3 x 50 ml of cold distilled water was used to wash the remaining sample. The sample was dried in an oven at >100°C. The conversion of the sample is defined by (W_0-W_1)/W_0 x 100 %. substrate $= \frac{W0-W1}{W0}$ x100%Where W_0 represents the initial weight of the sample and W_1 represents the weight of the remaining sample. The experiments were repeated at least 2 times and the data were averaged.

3. Results

3.1 Experiments on pure PET fibers

The initial experiments focused on the depolymerization of PET in ethylene glycol (glycolysis) to form smaller oligomers that can easily be separated from remaining cotton. It was expected that the smaller oligomers dissolve in the ethylene glycol solvent and by this the PET can be separated from the cotton by filtration. Ideally, high fractions of the monomer BHET should be formed, but the separation of PET and cotton was the major goal in the beginning. The separation was expressed with the conversion of PET that is, the weight lost of the sample.

The glycolysis of PET with ionic liquids as catalysts is an ideal reaction for the pretreatment of cotton / PET blends, due to the good recovery of the catalysts and the high yields of BHET

monomers achieved in literature. The setup for the glycolysis reaction was as described above. First, PET fabrics were tested as substrates for the depolymerization reaction, but no significant glycolysis could be observed (table 1, entry 1 and 2). When unraveled material (Texperium, The Netherlands) was used (picture 1A), clear depolymerization of PET was noticed. This was attributed to the bigger contact area for attack of catalyst and ethylene glycol. When the unraveled material was heated for 6 hours in ethylene glycol without any catalyst present, 12 % of the PET was depolymerized into smaller oligomers that dissolved in the ethylene glycol (entry 3). Due to the good results of PET depolymerization with ionic liquids in literature, 5 w/w% of 1-butyl-3-methyl-1H-imidazol-3-ium bromide ([bmim]Br was added to catalyse the glycolysis reaction. However, the conversion of PET to soluble smaller oligonucleotides was not much better (15% conversion, entry 4).

In literature, it was described that the basic ionic liquid [Bmim]OH gives higher conversions of PET and that the yield of the monomer BHET is good, as well [6]. For that reason, the experiment was repeated with equimolar amounts of [Bmim]Br and sodium hydroxide (NaOH). This combination produces the basic ionic liquid *in situ* and can act as an indication for a beneficial effect for the combination of a base and ionic liquid. Clear acceleration of PET glycolysis was observed in presence of NaOH and interestingly, it was possible to notice by eye that the substrate fibers were depolymerized into smaller pieces (entry 5, picture 1B). The conversion was determined to be 73%. As a next step, it was investigated if the ionic liquid actually contributes to the catalytic effect. In a control experiment with only NaOH as catalyst in the glycolysis reaction, 87% conversion was found (entry 6). In that case, it seemed that glycolysis of PET was at least as efficient as with the ionic liquid present, which means that the ionic liquid has - in this case - no effect on the conversion of PET to smaller oligomers. If the ionic liquids facilitates higher yields of the BHET monomer will be investigated at a later state.

Table 1 PET depolymerization reactions with pure samples[a]

Entry	Temperature (°C)	[bmim]Br (w/w%)	NaOH (w/w%)	Conversion (%)
1[b]	190	-	-	≤5
2[b]	190	5	-	≤5
3[c]	190	-	-	12
4[c]	190	5	-	15
5	190	5	1	73
6	190	-	1	87
7	190	-	2	99
8	180	-	2	81
9	160	-	2	27
10	160	-	5	58
11[d]	190	-	2	8

[a] Experiments following the representative procedure. [b] 2g of textile fabric, 40 ml ethylene glycol, for 4 hours, [c] 6 hours reaction time, [d] fine cotton material as substrate (picture 1C) instead of PET

Picture 1. A) unraveled pure PET material, B) smaller PET fibers on filter paper, C) fine cotton D) recovered fine cotton from self-mixed samples on filter paper, E) recovered cotton from unraveled cotton / PET post consumer waste.

When 2 w/w% of NaOH was added, 99% of all PET material was soluble in ethylene glycol at the end of the reaction (entry 7). This showed that complete depolymerization of PET from unraveled post consumer waste textiles can be achieved with a simple base as catalyst. To investigate the effect of the temperature on the conversion, the reaction with 2 w/w% of NaOH was repeated at 180°C. The conversion was 81%. At 160°C only 27% of the PET was converted. These results showed that lowering the temperature slows down the depolymerization and gives rise to lower conversions of PET. However, the effect of the lower temperatures can be counteracted by the addition of more catalyst. With 5 w/w% NaOH, at 160°C, 58% conversion was achieved.

3.2 Cotton / PET mixtures

With the best conditions, that are 190°C and 2 w/w% NaOH, the recovery of cotton from self-mixed samples was tested. Three samples with different ratios of fine cotton (picture 1C) and PET were prepared and processed under the optimized conditions. From sample A that contained 25% fine cotton before treatment 24% cotton was recovered. 48% out of 50% was recovered from sample B and in the case sample C where 75% of cotton was mixed with PET fibers, 72% of the cotton was recovered (picture 1D).
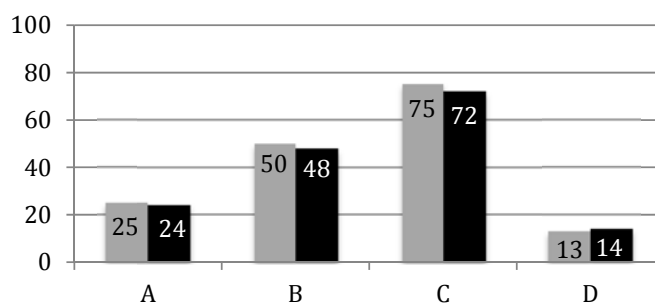
Graph 1. Recovered cotton from self-mixed cotton / PET samples A-C and post consumer waste B (in %). Grey column, fraction of cotton in the cotton / PET mixture. Black column, recovered cotton after the depolymerization of PET.

For unraveled cotton / PET blend post consumer waste the cotton content was determined as described in the materials and methods part prior to the depolymerization. From this procedure it was determined that the post consumer waste contained on average 13% cotton. Interestingly, after the glycolysis treatment an average of 14% intact material was recovered form the reaction mixture (graph 1, E). This was the cotton previously integrated in the cotton / PET blend.

4. Conclusions and Perspectives

Separation of cotton from cotton / PET blends is possible by selective depolymerization of PET using a simple basic catalyst (NaOH). The best conditions at a liquor ratio of 1:20 were found to be 190°C and 2 w/w% NaOH for 2 hours. At these conditions, the unraveled PET material was completely depolymerized and was easily separated from the cotton by filtration.

With premixed cotton / PET samples it was possible to demonstrated that almost all cotton can be recovered from cotton / PET blends after the depolymerization of PET.

In a follow up study, the selective formation of the depolymerization monomer BHET will be investigated, to see if this can be recovered in high yields, to be reused as starting material in PET production or other industrial processes. Furthermore, methods to recover all utilized chemicals will be developed to create a sustainable process.

Acknowledgements

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