Final report

Utsortering av bioplaster från återvinningsströmmen av konventionella plaster - en nödvändighet?

Separation of bioplastics from the waste stream of conventional plastics – a necessity?

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Summary

Biopolymers are presently produced in small volumes. However, in future, volumes may increase substantially. This may lead to contamination. This project studies what happens when bioplastics contaminate conventional plastic. Three conventional plastics were selected for this study: polyethylene (PE), polypropylene (PP) and polyethylene terephthalate (PET). In order to simulate contamination, two biopolymers, either polyhydroxyalkanoate (PHA) or thermoplastic starch (TPS) were blended in to the conventional polymers. A relatively large amount of tests have been conducted and tests show that PE is relatively robust again contamination, while polypropylene (PP) is somewhat more sensitive and polyethylene terephthalate (PET) can be quite sensitive towards contamination.

Background

The usage of bioplastics is expected to increase in future. Bioplastics, being both renewable and biodegradable, are very attractive and plastics such as TPS and PHA have been studied extensively [1-5]. The volumes of these bioplastics are presently small but expected to increase. The introduction of bioplastics on the market is however not without complications. For mechanical recycling, it is essential to sort the different plastics before they can be recycled. Even if the bioplastics are sorted out, some bioplastics will inevitably be incorrectly sorted, contaminating the waste streams of conventional petroleum based plastics. One concern is that the bioplastics are degraded and that the properties of the recycled plastics are seriously impacted. This concern was raised in a debate article in Dagens Industri a few years ago [6]. If bioplastic are truly a threat to the recycling industry, it is important to get knowledge about this. On the other hand, it is equally important that the development of the bioplastics is not hampered by misconceptions and incorrect assumptions.

The purpose of this project is to investigate to what extent a small contamination of bioplastic may have on the properties of conventional petroleum based plastics. The project consists of three parts: part I, compounding of small amounts of bioplastics into conventional plastics; part II, influence of humidity, and part III, repeated processing.

Experimental

Two bioplastics were selected, thermoplastic starch (TPS) and polyhydroxyalkanoate (PHA). PHA (PH326300 from Goodfellow) was a commercial grade obtained from Sigma-Aldrich. Starch is by itself not thermoplastic and a TPS blend was prepared according to the literature [7]. Shortly, starch was first plasticised with glycerol and then compounded with polylactic acid. Three conventional plastics were selected for the experiments: high density polyethylene (PE, GA7760, Purell), polypropylene (PP, Moplen HP 648 T, LyondellBasell) and polyethylene terephthalate (PET, Arnite A06 700).

The conventional plastics where compounded with the 0%, 1% and 5% of the bioplastics. The compounding was done on a 15 ml micro-compounder (DSM, Holland) according to the manufacturers recommendations. Test bodies were produced after the compounding using laboratory injection moulder (DSM, Holland). Recycling of the materials (ie. Repeated processing) was simulated by injecting the materials to the same microcompounder and processing the materials for an extended time (2, 20 and 60 min). The degradation of the polymer was characterised by DSC as described below. Experiments with humidity were done by first conditioning the samples in a climate chamber and then processing the plastics as described above. Samples were conditioned at 85% RH for 72 h.

The prepared test bodies were characterised by tensile testing. The tensile strength was determined at a speed of 30 mm/min using a tensile tester from Tinius Ohlsen (England) and the modulus was determined at 1 mm/min. Charpy impact tests were conducted according to ISO 179 using a Charpy impact tester from Cometech 639D (Taiwan). PP and PET were tested without notching while PE was tested with notching. The thermal properties of the prepared samples were tested by differential scanning calorimetry (DSC) using a Q2000 (TA Instruments, USA). About 10 mg were heated at 10°C/min in an atmosphere of nitrogen gas.

Scanning electron microscopy (SEM) was conducted by an external laboratory.

Resultat

Part I – Simulation of contamination

In the first part of the project, small amounts (0,%, 1% and 5%) of bioplastics were compounded with the conventional plastics in order to simulate a contamination. The result of the tensile testing is shown in table 1. The tensile testing showed that for PE, tensile strength and modulus was almost unaffected of the contamination. The elongation is however clearly reduced, meaning that the material is becoming more brittle after the compounding. This is an expected result. Generally, it can be said that PP is somewhat more sensitive to the contamination than PE. This can be explained by the fact that the melting point of PP is higher than for PE and as a consequence, the biopolymer will degrade more quickly. However, the reduction of the tensile properties for PP is relatively modest. It is also important to notice that when plastics are recovered, there will always be a contamination that will reduce the material properties. The reduction of the tensile properties is not necessary larger than if a non-biodegradable polymer had contaminated PE or PP. The Charpy impact strength is shown in Table 2 and it can be seen that the Charpy impact strength is generally a more sensitive test method towards contamination. Again, PE is relatively unaffected by the contamination but for PP there is a relatively large reduction of the impact properties already at 1% contamination.

PET is a polyester and it is by its very nature more sensitive to degradation than PE and PP. PET also have a much higher melting point than PE and PP and as a consequence, the biopolymer will quickly degrade at the processing temperature of PET. As for the tensile strength, PET can tolerate 1% contamination without any reduction of the tensile strength. However, when the impact strength is examined, it is clear that already at 1% contamination that there is a strong reduction of the properties. It can also be seen that the presence of TPS is more detrimental to PET than PHA is. This can be explained by the fact that TPS contain reactive hydroxyl groups that can react with the ester bond of PET. This will in other words lead to degradation of PET.

Table 1. Summary of the tensile testing. The standard deviation is shown within brackets.

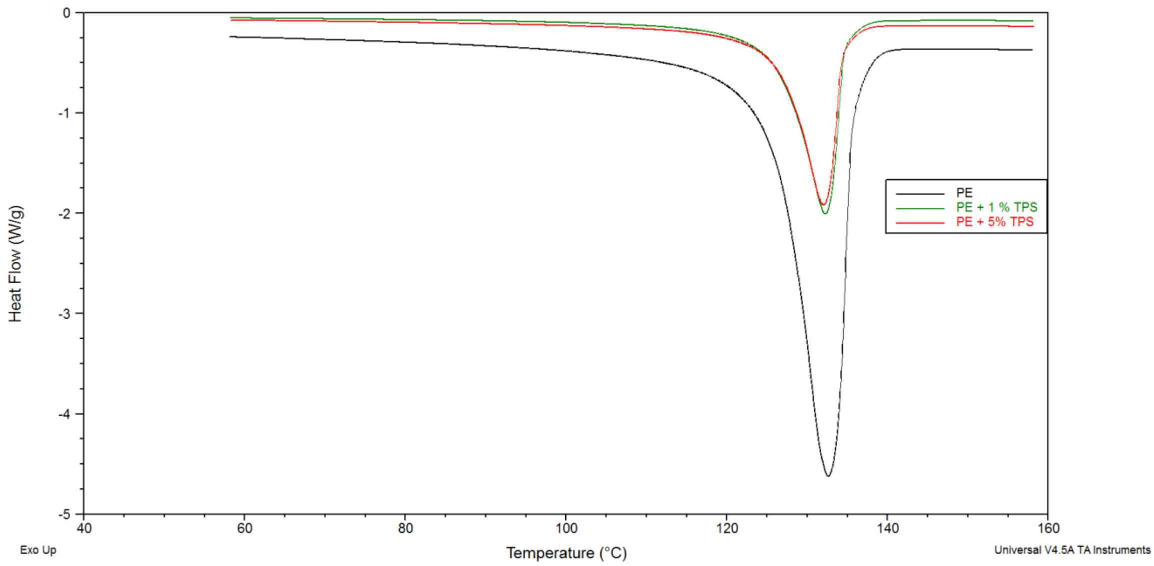
Polymer blend	**Tensile strength at break (MPa)**	**Modulus (GPa)**	**Elongation at break (%)**
PE	29.4 (0.2)	1.1 (0.3)	1319 (308)
PE + 1% TPS	27.4 (0.8)	1.2 (0.1)	237.7 (168)
PE + 5% TPS	28.4 (1.2)	1.1 (0.1)	150.6 (56.8)
PE + 1% PHA	27.9 (1.1)	1.2 (0.1)	719 (82)
PE + 5% PHA	29.4 (1.4)	1.3 (0.0)	480 (304)
PP	42.3 (2.0)	1.8 (0.1)	898 (137)
PP + 1% TPS	35.9 (1.7)	1.7 (0.1)	646 (36)
PP + 5% TPS	34.6 (2.5)	1.7 (0.1)	281 (219)
PP + 1% PHA	34.7 (1.5)	1.9 (0.1)	689 (36)
PP + 5% PHA	37.1 (1.9)	1.7 (0.1)	636 (32)
PET	66.0 (2.8)	2.7 (0.1)	22.1 (7)
PET + 1% TPS	65.0 (3.9)	2.6 (0.1)	6.1 (0.7)
PET + 5% TPS	26.9 (4.5)	2.8 (0.1)	2.4 (1.1)
PET + 1% PHA	78.8 (4.7)	2.7 (0.1)	8.1 (1.4)
PET + 5% PHA	28.6 (5.7)	2.9 (0.1)	2.8 (0.6)

Tabell 2. Summary of the Charpy impact testing. The standard deviation is shown within brackets.

Polymer	**Charpy impact strength(kJ/m^2)**
PE	3.0 (0.5)
PE + 1% TPS	3.1 (0.6)
PE + 5% TPS	3.1 (0.5)
PE + 1% PHA	2.8 (0.3)
PE + 5% PHA	2.4 (0.6)
PP	56.0 (21.1)
PP + 1% TPS	33.5 (8.5)

PP + 5% TPS	20.7 (3.8)
PP + 1% PHA	54.7 (3.1)
PP + 5% PHA	44.8 (4.9)
PET	62.8 (29.8)
PET + 1% TPS	11.6 (2.6)
PET + 5% TPS	3.3 (0.9)
PET + 1% PHA	31.2 (17.9)
PET + 5% PHA	10.3 (6.0)

The thermal properties of the compounds were also characterised by thermal tests by DSC. One example is shown is Figure 1 where neat PE is compared to 1% and 5% contamination. The melting point at about 130°C can be seen and the area is a measurement of the crystallinity. As a general conclusion it can be said that the plastics become less crystalline when contaminated. This is expected and the reduced crystallinity is caused by the contamination disturbing the crystallisation process. The peak of the melting point is relatively unaffected by the contamination.



Figur 1. Characterisation by DSC of neat PE (black curve, bottom), with 1% TPS (green curve) and with 5% TPS (red curve).

Table 3. Summary of the characterisation by DSC. The standard deviation is shown within brackets.

Polymer blend	**Crystallinity (%)**	**Peak of the melting point (°C)**
PE	77.1 (3.5)	132.7 (0.0)
PE + 1% TPS	27.4 (2.3)	132.5 (0.3)
PE + 5% TPS		
PE + 1% PHA	25.5 (4.1)	132.1 (0.3)
PE + 5% PHA	23.6 (3.6)	132.1 (0.1)
PP	49.9 (4.4)	163.5 (0.4)
PP + 1% TPS	16.8 (1.3)	162.1 (0.4)
PP + 5% TPS	16.7 (0.4)	161.5 (0.2)
PP + 1% PHA	12.0 (1.3)	161.2 (0.1)
PP + 5% PHA	18.7 (0.0)	161.8 (0.4)
PET	24.1 (2.3)	254.0 (3.2)
PET + 1% TPS	10.4 (2.3)	254.4 (0.1)
PET + 5% TPS	14.9 (1.7)	251.6 (0.5)
PET + 1% PHA	12.3 (0.7)	254.7 (0.3)
PET + 5% PHA	15.3 (0.9)	256.0 (0.6)

The blends were also characterised by SEM and examples are shown in Figure 2 where neat PE is compared to PE + 5% TPS. A biphasic morphology can be seen showing that, as expected, the two polymers are not truly blendable. Furthermore, it appears that while the dispersion is good, the adhesion is not optimal between the polymers as splits can be seen. This further contributes to reduced mechanical properties.

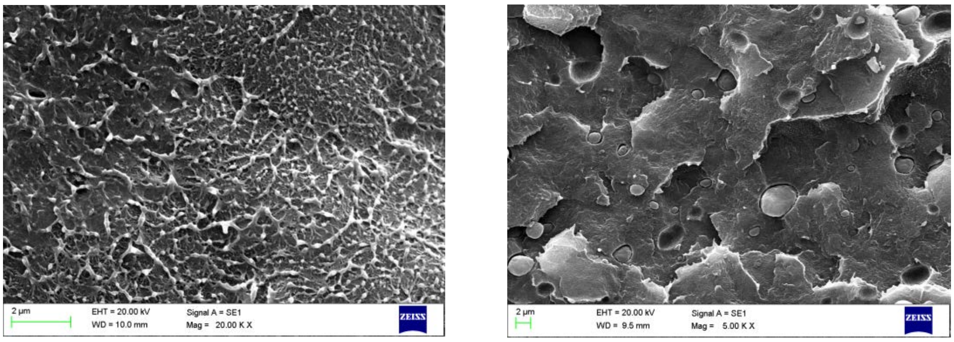


Figure 2. SEM micrographs of neat PE and PE + 5% TPS.

Part II – influence of humidity

In part two, the influence of humidity was studied. The background to this study is as follows. When plastics such as PE and PP are processed in the industry, they are never dried before processing since they are not hygroscopic. However, if a conventional plastic is contaminated by a bioplastic, the bioplastic may absorb water. The water may then react and degrade the biopolymer when processing. This could potentially lead to an increased degradation.

The result of the tensile testing is shown in Table 4. Tests show that, under the chosen conditions, the humidity didn't cause any reduction of the tensile properties. On the contrary, possibly the tensile strength increased somewhat but the increase is not so significant considering the standard deviation.

Table 4. Characterisation by tensile tests before and after conditioning with humidity. The standard deviation is shown within brackets.

Polymer	**Tensile strength (MPa)**	**Elongation (%)**	**Modulus (GPa)**
PE/TPS5 (without conditioning)	28.4 (1.2)	10.5 (0.3)	1.2 (0.1)
PE/TPS5 (with conditioning)	31.4 (0.6)	10.5 (0.9)	1.5 (0.1)
PP/TPS5 (without conditioning)	34.6 (2.5)	10.9 (0.9)	1.7 (0.1)
PP/TPS5 (with conditioning)	38.0 (1.2)	10.4 (0.5)	2.1 (0.3)

Part III – Recycling of contaminated materials

In the third part of the project, it was studied what happens if a contaminated polymer is recycled. Two material combinations where selected, PE and PP contaminated with 5% PHA. The repeated processing was simulated by continuously processing the materials for up to 60 minutes. Assuming a processing time of 2 min for each recycling time, this would correspond to 30 times of recycling.

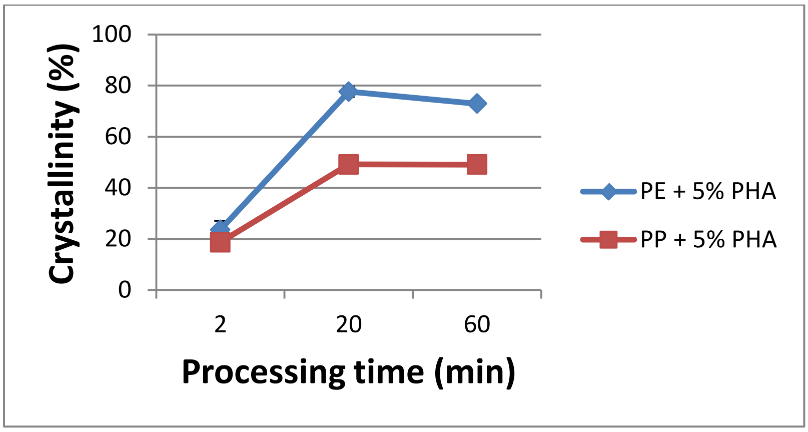


Figure 3. Simulation of the repeated processing by measuring the crystallinity as a function of the processing time.

Test show that the crystallinity increased by increasing processing time. This means that when the polymers are processed, polymer degradation occur causing the polymer chains to gradually become shorter which will enhance the crystallisation process. In previous studies, PE has shown to be indeed very stable against repeated processing. In a previous study, repeated processing of neat PE was simulated under similar conditions [8]. After 200 min of continuous processing, the crystallinity was almost unaffected. This clearly demonstrates that the contamination of the biopolymer affect the recyclability of the material. However, from an industrial perspective, it would be enough to be able to recycle the contaminated polymer a couples of time, and this shouldn't be a problem.

Dissemination

The results will be spread by both a peer-reviewed article and through a conference:

- One manuscript has been written, "Effect of small amount of thermoplastic starch on the mechanical recycling of conventional plastics", which will be sent to *Journal of Polymers and the Environment* for peer-review.
- The results will also be presented at a conference, 21st International Conference on Waste Management, Recycling and Environment Barcelona, Spain.

Conclusions

The volumes of bioplastics may increase in future. The waste streams of conventional plastic will then be contaminated by biopolymer to some extent. This project has investigated to what extent this may influence the material properties and can be summarised as follows:

- PE is presently the most commonly recycled plastic. Test shows that PE is relatively unaffected by addition up to 5% biopolymer. This is a relatively high contamination. The contamination was mainly seen as a reduction of the elongation at break.
- PP is somewhat more sensitive towards contamination and this was reflected mainly by decreased impact properties while the tensile properties were relatively unaffected.
- PET is a polyester and intrinsically more sensitive to polymer degradation than the two polyolefins. It is clear from our tests that PET is sensitive towards contamination. However, presently PET is mainly recycled as PET bottles and TPS and PHA are usually not used for this application.

When polyolefins, such as PE and PP, are recycled they will inevitably become contaminated by other petroleum based plastics. The will lead to impaired mechanical and thermal properties. The reduction in thermal and mechanical properties seen in this study is not necessarily larger just because the contaminating polymer is biodegradable. Finally it is also important to remember that recycled plastics are rarely used alone in the industry but rather mixed with virgin plastics.

In conclusion, it will obviously be necessary to separate bioplastics in future, but, for PE and PP that account for more than 50% of all conventional plastics, a small contamination should not be a major problem.

Economic report

Below is the outcome for the project presented with the amounts of salary costs, material costs and analysis costs.

Type	Amount (SEK)
Salary costs (incl. OH costs)	261804
Materials	14198
External analysis	2550
Dissemination (conference, manuscript)	21828
Total	300380

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