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Biobased, thermoreversibly crosslinked polyesters

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Chapter 6

Closing the chain: a technological assessment

6.1 Introduction

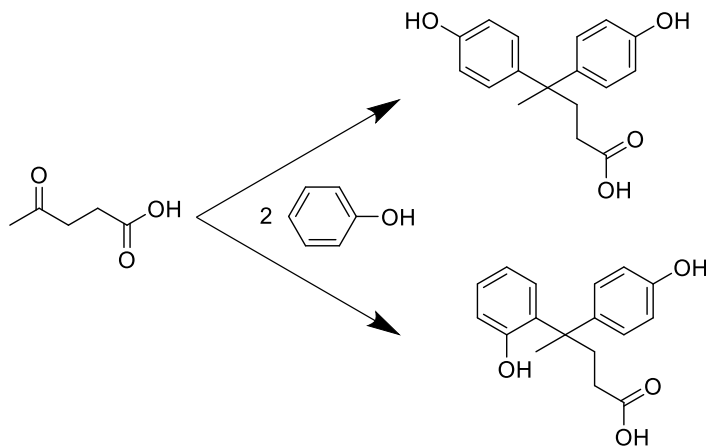
Throughout this thesis a route has been laid out for the synthesis of a biobased, reversible thermoset-like material able to be reprocessed and reworked like a thermoplastic. Various steps have already been taken successfully: the functionalization of DPA, its subsequent copolymerization and successful thermoreversible crosslinking. However, other important steps must be taken when making allowances for the full chain, i.e. from biomass to final product. This assessment will address two parts: the first part will, deal with the first reaction in the whole process: the synthesis of diphenolic acid itself from levulinic acid and phenol. While both of these starting materials are obtainable from renewable resources, the currently employed process which combines them could be greatly improved from a sustainability viewpoint as the current commercial process consists of homogeneous catalysis in the form of dissolved Brønsted acids¹⁻³. The application of a heterogeneous catalyst would hold various obvious benefits such as facile catalyst removal and recovery.

The second part of this assessment will discuss the application of the thermoreversible material in a real-life application. In their pure form, the polymers described in this thesis show excellent reworkability, reprocessability and recyclability. However these materials are rarely used in their pure form. In order to either reduce costs or improve the mechanical properties of the final product, thermosets are often blended with fibrous materials. To test the viability of this material, blends were prepared with fibrous materials. In line with the philosophy of this work, only fibers obtained from renewable resources were employed.

6.2 Part 1: DPA synthesis using heterogeneous catalysis

The currently employed process for the synthesis of diphenolic acid from levulinic acid utilizes dissolved Brønsted acids. The implementation of a heterogeneous catalyst holds many potential merits such as catalyst reusability. Fortunately, these merits have been recognized and previous publications describe the synthesis and application of various heterogeneous catalysts for the synthesis of diphenolic acid. Furthermore there are significantly more catalysts described for the (very similar) synthesis of bisphenol A, providing an even larger knowledgebase. All reported catalysts are rated based on three aspects: activity, selectivity and stability. The selectivity of the reaction is negatively affected by the formation of an unwanted isomer during the reaction. This isomer is obtained due to the fact that phenol can react with levulinic acid in two positions of the phenolic ring: ortho and para (Scheme 1). The *o,p*-isomer is unwanted as the *p*-OH group is unavailable for further reactions due to steric hindrance. Stability is not often addressed in detail, however some publications^{4-6,6} mention the possibility of repeat experiments after a catalyst regeneration step.

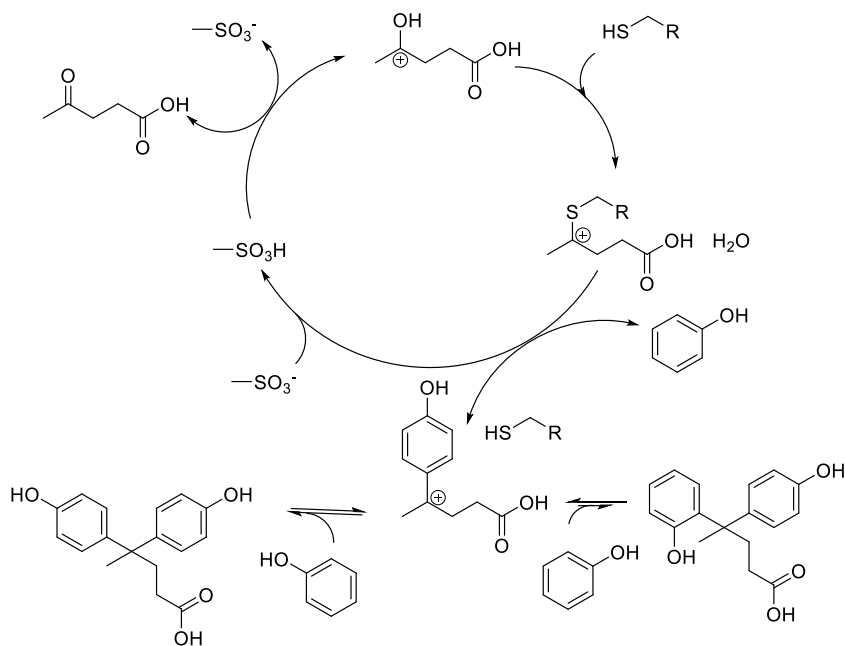
Scheme 1: *o,o*-isomer (top) and *o,p*-isomer (bottom) of DPA condensation reaction



It is widely accepted that the synthesis of DPA benefits from strong Brønsted acidity and, although not fully understood, that the presence of thiols in the reaction mixture has a favorable effect on the ensuing selectivity. Various mechanisms have been proposed about the exact role of the thiol, mostly assuming its role to be mostly based on steric hindrance driving the selectivity.

However van de Vyver *et al.* report⁷ significantly reduced activity and selectivity when changing the cocatalyst from ethanethiol to 1,1-dimethylethanethiol under otherwise identical conditions. This has led them to propose the mechanism depicted in Scheme 2.

Scheme 2: proposed mechanism for DPA synthesis involving thiols as cocatalyst



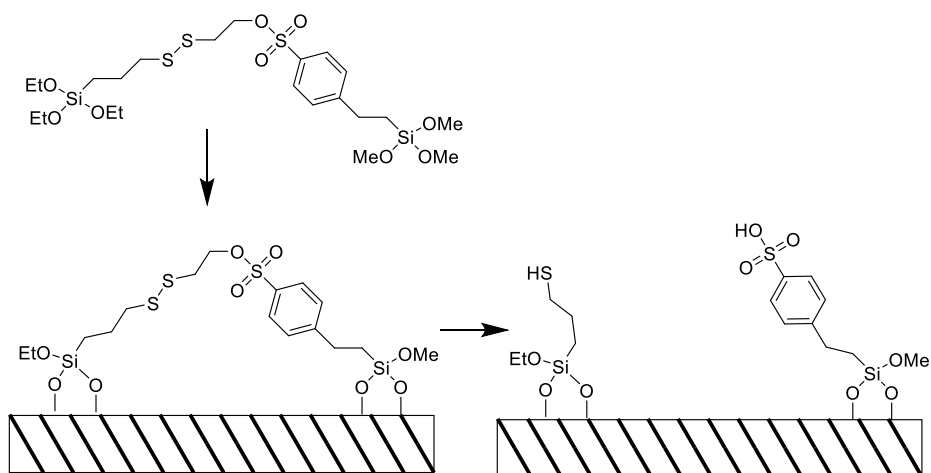
Various systems have been described as potential candidates for the role of heterogeneous catalyst: sulfonation of carbon, giving strong Brønsted acidity on a heterogeneous carrier⁸; zeolite materials^{1,9}; immobilization of bifunctional precursor resulting in a proximity effect of thiol and acidic group¹⁰; immobilized heteropolyacids on Cesium^{6,11}, silica⁵ or clay¹², etc. ...

The use of a sulfonic acid group immobilized on carbon is a very straightforward implementation of strong Brønsted acidity and can easily be complemented with thiol functionalities as well, which should greatly enhance selectivity and activity. Unfortunately the material suffers from leaching of the acid group, significantly reducing its activity over the course of multiple cycles. The immobilization of a bifunctional precursor onto silica is a very elegant concept based on the assumption that proximity of thiol and Brønsted acid groups promotes the

selectivity of the reaction even further. The procedure is depicted in Scheme 3. Unfortunately, despite the elaborate synthesis, the authors report only a relatively small effect on selectivity¹³.

Finally, heteropolyacids (HPAs) hold great promise as these have been used with great success in the synthesis of bisphenol A^{11,14}. Furthermore, a positive effect on yield and selectivity was observed upon implementation of diethylaminothiol (DEAT) as co-catalyst⁷. Some results have already been reported using immobilized HPAs of both Keggin ($H_3PW_{12}O_{40}$)⁵ and Wells-Dawson ($H_6P_2W_{18}O_{62}$) types⁶ of HPAs, but the effect of using DEAT as co-catalyst has not been explored just yet for the synthesis of DPA. HPAs hold great promise mainly due to their strong acidic character, although the exact acidity (pKa) cannot be given despite having been thoroughly studied¹⁵. They can be immobilized in various ways, i.e. on silica⁵, clay¹² or cesium¹¹ giving them excellent heterogeneous catalyst properties.

Scheme 3: Immobilization and activation of the difunctional precursor



In order to assess the potential of HPA-based systems, various compounds have been synthesized (Table 1), some of which already known to work for the synthesis of DPA (entries 4,5 and 6), others are only known to be active in the synthesis of BPA (entry 9), and finally some combining different positive improvements such as substituting W12 for W18 and the addition of DEAT(entries

7 and 10 respectively). W12 and amberlyst were used as homogeneous and heterogeneous reference respectively.

Entry		Conversion ^a	Yield ^b	Selectivity (pp')	Ref
1	HCl	65% LA		68.75	4,5,16
2	W12	60 % LA	30 % DPA	74%	6
3	Amberlyst	33.8 % LA	17% DPA	80 %	7,17
4	CsW12	28.3 % LA	27% DPA	80.4 %	4,5,16
5	CsW18	35.9 % LA	35% DPA	88%	6
6	SiO ₂ -W12	80 % LA	35% DPA	75%	4,5,16
7	SiO ₂ -W18	n.r. ^c	n.r. ^c	n.r. ^c	
8	CsW12	85% AC ^d	34%	40 % pp	14
9	CsDEATW12	95 % AC ^d	94%	96 % pp	14
10	CsDEATW18	n.r. ^c	n.r. ^c	n.r. ^c	

Table 1: Conversion, yield and selectivity (where available) for catalysts screened

^a %LA = levulinic acid conversion (for DPA synthesis), %AC= acetone conversion (for BPA synthesis)

^b No specification given on max possible yield

^c System not reported

^d System reported active for BPA synthesis

6.3 Experimental section

Levulinic acid, phenol, Tetraethyl orthosilicate (TEOS), 12-tungstophosphoric acid (H₃PW₁₂O₄₀), Cs₂CO₃ (99%), 2-diethylamino-ethanethiol hydrochloride, amberlyst, N-Methyl-N-(trimethylsilyl)trifluoroacetamide and P123 (MW 5800) were obtained from Sigma-Aldrich and used as received.

W18 was synthesized as described in¹⁸. SiO₂-W₁₂ and SiO₂-W₁₈ were synthesized according to the procedure described previously⁵. The heteropolyacid cesium salts CsW₁₂ and CsW₁₈ were prepared according to the method described in⁶, and successively functionalized with DEAT according to the procedure described in¹⁴

The condensation reaction was performed in a glass vessel sealed with a teflon cap and equipped with a magnetic stirrer at 100°C. The vessel was charged with phenol (1.28 g, 13.6 mmol) and Levulinic acid (0.395 g, 3.4 mmol), as well as 50

mg of catalyst. The mixture was stirred at a speed of 1200 rpm and the reaction time was set at 6, 8 or 24 hours and samples were taken during the reaction to track the conversion of the reagents.

6.3.1 Analysis

Samples were analyzed with a GC-MS (HP 6890 Series and HP 5972 Series, respectively). The column used was a Restek Rxi-5sil MS, with a length of 30.0 m, a diameter of 250 μm and a film thickness of 0.25 μm , using a split injector (ratio 50:1) and column flow of 0.8 ml/min and an injection temperature of 250°C.

The samples were prepared by adding 1 μl of reaction mixture to 1 ml THF with naphthalene (internal standard). To this mixture, between 20-30 μl of MSTFA (N-methyl-N-(trimethylsilyl)trifluoroacetamide) was added to silylate the products (phenol, levulinic acid and DPA) which was necessary in order to enable analysis by GC.

6.4 Results:

6.4.1 Elemental analysis of catalysts: calc. (found):

SiO₂-W12: Si: 37.33% (31.99%; 31.38%) P: 0.22% (0.0078%; 0.0155%)

SiO₂-W18: Si: 37.33% (35.06%; 34.24%) P: 0.28% (0.0638%; 0.1485%)

CS_{2.5}H_{0.5}PW₁₂O₄₀: Cs: 10.35% (9.54%; 10.12%)

CS_{1.5}H_{4.5}P₂W₁₈O₆₂: Cs: 4.37% (4.00%; 3.95%)

CS_{2.5}H_{0.25}DEAT_{0.25}PW₁₂O₄₀: N: 0.12% (0.12%; 0.13%) C: 0.56% (0.59%, 0.65%) H: 0.12% (0.18%, 0.16%) S: 0.25% (0.16%, 0.14%)

CS_{1.5}H_{2.25}DEAT_{2.25}P₂W₁₈O₆₂: N: 0.69% (1.18%; 1.26%) C: 3.33% (6.39%, 6.44%) H: 0.74% (1.49%, 1.46%) S: 1.48% (2.57%, 2.74%)

6.4.2 Activity:

The activity was determined from the conversion of levulinic acid and compared to the values reported previously (where applicable) (Figure 1). Unfortunately the method of analysis employed was not able to distinguish between both potential

isomers meaning no conclusions could be drawn about the selectivity of the catalysts.

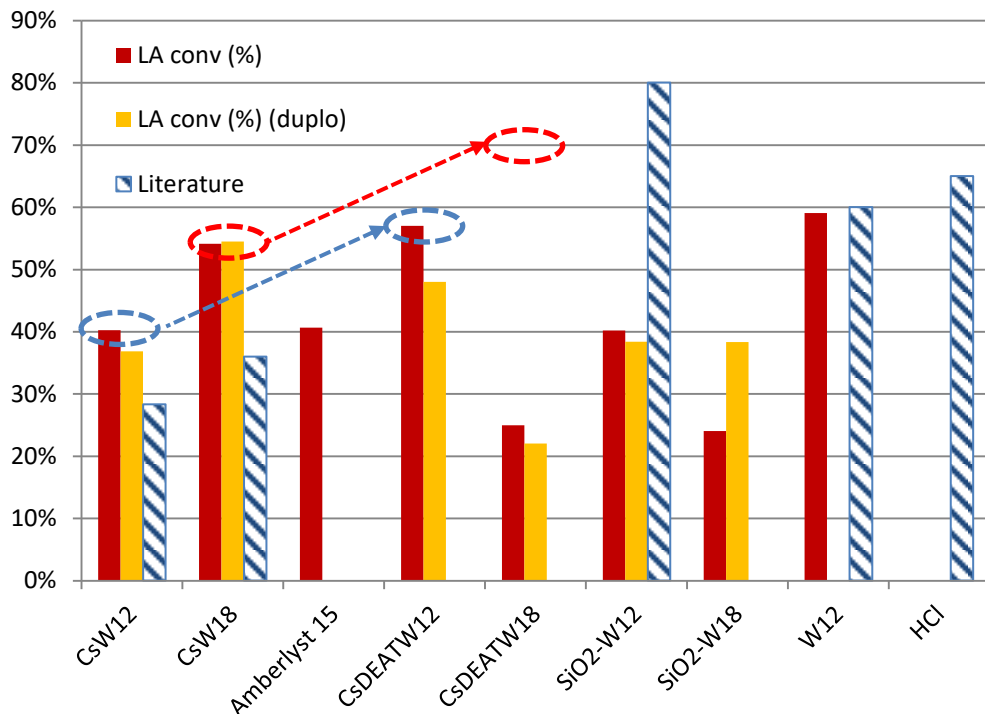


Figure 1: Activity towards the synthesis of DPA for the catalysts screened in this research

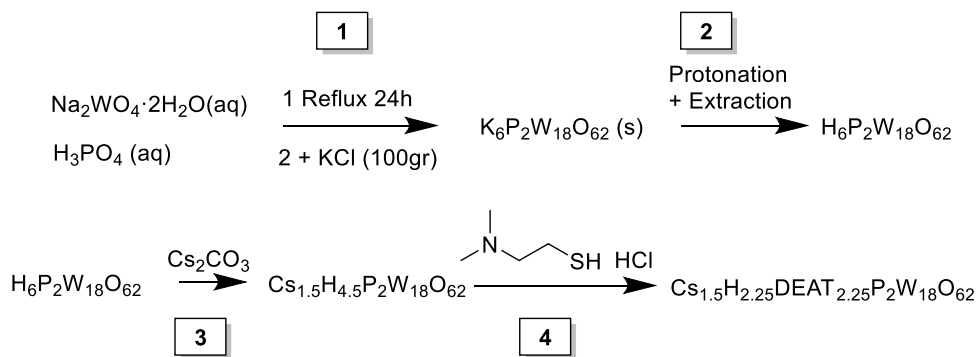
As expected the activity of amberlyst 15 is significantly lower than the homogeneous systems. Furthermore, the use of W12 as homogeneous catalyst unsurprisingly gives results very similar to that of hydrochloric acid¹⁶. Also nearly identical conversion compared to reported values⁶ have been obtained, indicating good reproducibility (dashed blue bars in Figure 1).

The same cannot be said about the silica-based systems, however: it proved difficult to reproduce the catalyst following the procedure described⁴. Elemental analysis showed that both the W12 and W18 variant showed virtually no presence of phosphorous, indicating failed immobilization of the HPA. This is reflected in the activities obtained.

Cesium immobilization of both W12 and W18 has been successful, giving excellent activities compared to reported values. The direct comparison with published activities is somewhat skewed however, as the selectivity of the system could not be determined. There is a notable effect discernable for the addition of DEAT to the CSW12 catalyst: an increase in conversion of roughly 15% was observed (blue dashed arrow in Figure 1) when comparing CsW12 and CsDEATW12. When looking at the CSW18 system this effect is not present however. (The expected increase in activity is depicted by the red dashed arrow)

The elemental analysis of CSDEATW18 showed a larger than expected amount of sulfur present in the material. This can be explained by taking a closer look at the synthetic procedure, depicted in Scheme 4. The first step consists of isolation of the intermediate as potassium salt (Scheme 4-1). This salt is then acidified and extracted as ether-adduct giving the desired W18 (Scheme 4-2). The next step consists of immobilization of the W18 on cesium carbonate by replacing part of the available protons (Scheme 4-3). Finally half of the available protons are replaced by DEAT (Scheme 4-4).

Scheme 4: Reaction scheme for the synthesis of CsDEATW18



Upon closer examination of the precursor via elemental analysis showed that the protonation step (Scheme 4-2) had been incomplete, yielding a material with a significantly reduced amount of available protons. (i.e. instead of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ the resulting material could probably be more accurately described as $\text{K}_2\text{H}_4\text{P}_2\text{W}_{18}\text{O}_{62}$). This error led to a final product which, rather than the desired 1:1 ratio of H:DEAT, contained a H:DEAT ratio of 0.06:1. Unfortunately, the procedure is rather complex, involving a multi-step synthesis, and while a likely culprit has been

identified in incomplete protonation, this is still an assumption. The results obtained by using CsDEATW12 are very promising however, and pave the way to further improvements. If a similar effect of the addition of DEAT is observed on the system based on W18, and the desired $\text{Cs}_{1.5}\text{H}_{2.25}\text{DEAT}_{2.25}\text{P}_2\text{W}_{18}\text{O}_{62}$ can successfully be synthesized, this would be a very promising candidate for a suitable and sustainable catalyst for the synthesis of diphenolic acid.

6.5 Part 2: Towards a real life application of a thermoreversible thermoset-like polymer: compounding with flax and jute fibers.

Upon application, many thermosetting resins are compounded with various additives such as pigments^{19,20}, flame retarding agents^{21,22} and/or filler materials. Fibrous fillers are very common as these can simultaneously reduce the weight and cost of the material while at the same time imparting desirable properties like improved (impact) strength to the material. For polyester resins the most commonly employed fibrous material is glass fiber. This trend is changing, however, as more and more initiatives are moving towards the use of sustainable fillers²³. Materials such as wood fibers²⁴, flax²², jute²⁵ and cellulose²⁶⁻²⁸ are being employed successfully. In order to evaluate the applicability of the thermoreversible polyester described in the previous chapters of this thesis compounds with fibrous materials have been prepared and tested. In order to preserve the sustainable nature of the material, the fibers used are all obtained from natural resources. Samples compounded with either flax or jute have been prepared containing 1%, 5% or 10% of the fibrous material (Figure 2). As the test bars were relatively small, the effect of inhomogeneity in the fibers has a significant effect on the outcome. It was therefore decided that in order to reduce this inhomogeneous nature the size of the fibers were reduced by freezing in liquid nitrogen, grinding using an industrial grinder and subsequently passed through a sieve tower. The fraction of 1-0.5 mm particle size was used in this experiment.

The polymer used for all samples was a furan functionalized polyester which was polymerized in the presence of a chain stopper (see chapter 3 of this thesis), the polymer (PE-fur) was used as a powder which was mixed with bismaleimide crosslinker in a ratio of maleimide to furan groups of 1:1. The fibers were mixed with the polyester and compounded in a hot press, both in T-bones and straight bars (Figure 3). Upon removing the samples from the mold the need for reinforcement became painfully clear as it proved challenging to remove the pure polyester samples intact: the high brittleness of the material ensured many cracks formed during this process. Nevertheless intact bars of all formulations were obtained. The fibers showed good dispersion throughout the material, and gave no signs of phase separation on the polymer/fiber interface.



Figure 2: Flax (left) and Jute (right) fibers used and fiber/polymer (PE-fur) mixtures (far right)

Unfortunately the brittleness of the polyester made measurements of its tensile strength impossible: the material would either slip from the clamps or crack due to the clamping force exerted upon it. This combined with a rather large experimental error gave rise to a very binary conclusion: the fact that tensile measurements could be successfully performed at all on samples containing fibrous reinforcements means that these are stronger than the unsupported base polymer. Any further quantification of this effect is unfortunately not possible from these results.

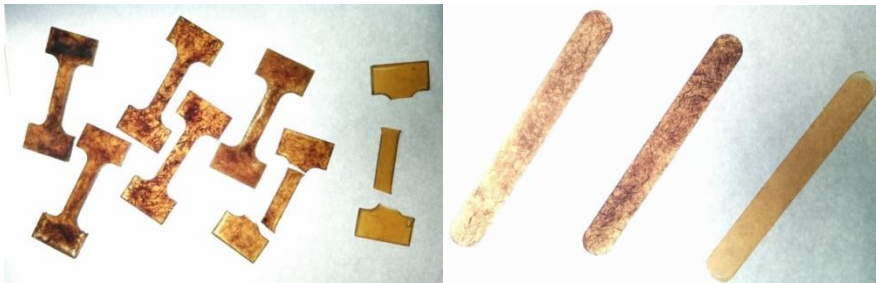


Figure 3: backlit photo of samples containing, left-to-right: 10%jute (2x), 10%flax (2x), 5%jute (2x), pure PE,10%jute, 10%jute, 1%jute

In an attempt to obtain some quantifiable idea of the reinforcing properties of the polyester/fiber compound samples consisting of layered flax mats filled with polymer were compressed in a heated press. The resulting material showed excellent penetration of the polymer (Figure 4). There was little to no delamination of the layers, as observed by manual strumming of the sample.

Tensile testing of the compound as well as the fiber mats were performed, and once again no quantitative analysis could be performed as the cured samples could not be broken by the tensile machine, withstanding 5 kN of force. This proves only conceptually that the polyester can be reinforced easily and effectively by the addition of fibrous filler materials.

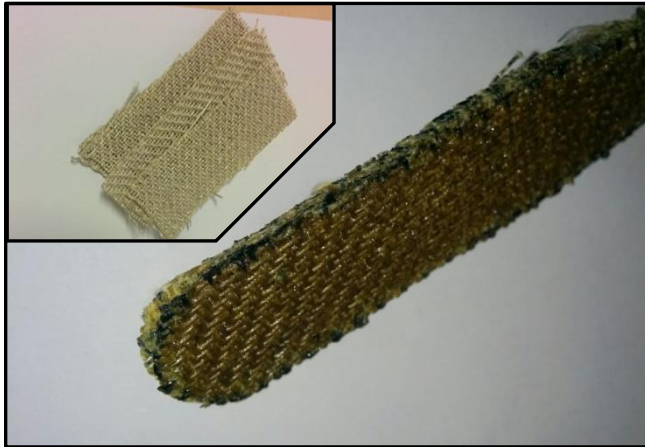


Figure 4: Flax fiber mat reinforced PE-fur composite, (inset) fiber mats used.

6.6 Conclusions

The possibility of compounding the polyester described in this thesis (PE-fur) with various renewable fibrous materials has been demonstrated by successfully obtaining samples containing various amounts of different fibers (i.e. flax and jute). This effectively yielded a nearly completely renewable composite, which is proven to be able to undergo thermoreversible crosslinking. Furthermore, when using flax mats good penetration of the polyester into the fiber mats was observed and the resulting material did not suffer from delamination, a common problem for layered composites²⁹. The exact (quantitative) effect of fiber reinforcements could not be established, unfortunately, as the virgin material could not be measured in the tensile testing machine.

6.7 Outlook

As stated in the conclusions of part 1, the synthesis of diphenolic acid from levulinic acid could greatly benefit from a heterogeneous catalyst. A very promising candidate would be the DEAT-functionalized, Cs-immobilized W18 heteropolyacid. Should the same increase in activity upon the addition of DEAT which was observed for the W12 system be obtained for the W18 system as well, a very potent system would be obtained.

Furthermore, as evident from part 2, the potential for property-enhancement through the application of fibrous filler materials is very high. The bio-based fillers tested display excellent compatibility with the base polymer and a significant increase in tensile strength, in fact when utilizing flax mats the tensile strength increase was so high that it was no longer possible to break the samples. This topic would benefit greatly from additional research. One area of interest could be the use of functionalized fillers where the fibrous materials are able to partake in Diels-Alder reactions with the polymer matrix.

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