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Title: Biomass based plasticizers from liquefied waste paper

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Abstract

The overall aim of the project was to design and develop new environmentally friendly plasticizers from non-edible biobased products such as waste paper. During the project white writing paper and brown paper towels were liquefied by acid catalysed hydrolysis in the presence of ethylene glycol and glycerol. The liquefaction efficiency was good for brown paper, but the process did not work well in the case of white paper. The liquefied products were characterized by NMR, ESI-MS, SEC and SEM and used as monomers for synthesis of biobased plasticizers. A potential high volume application for these esters would be as plasticizers for poly(vinyl chloride) (PVC). The synthesized plasticizers were, thus, blended with PVC by solution casting and the blends were characterized for their mechanical properties and miscibility by tensile testing, DSC and FTIR. The new plasticizers had similar or even better plasticizing efficiency compared to traditional diisooctyl phthalate plasticizer. Novel bio-based plasticizers with high environmental and economic potential were, thus, successfully designed from non-edible liquefied biomass.

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1. Introduction

Our society needs to change from oil-based to bio-based concerning both production of fuels and materials. During the last years the interest in producing environmentally friendly polymeric products from biomass has rapidly escalated. However, even the polymer additives and especially the high-volume ones such as plasticizers, should be bio-based, safe and environmentally friendly. In these efforts the use of different waste products is to be prioritised in order not to compete with food production. Several papers demonstrate liquefaction of wood flour and waste paper to polyols [1,2]. In most cases these polyols were used as raw materials for the synthesis of polyurethane based polymers [3,4] or phenolic type resins [5]. In one case polyesters were synthesized [6]. However, no application of liquefied wood flour or waste paper as plasticizer or plasticizer raw material was found.

A potential high volume application for these esters would be as polymer plasticizers. Poly(vinyl chloride) (PVC) is today one of the most important plastic materials in terms of consumption right after polyethylene and the consumption is increasing year by year due to the cheap price and unique properties of PVC. As an example about one third of disposable medical devices are manufactured from plasticized PVC and it represents the main thermoplastic (85%) in pre-sterilised single use applications. Flexible PVC grades are obtained by compounding PVC with plasticizers. The most significant group of PVC plasticizers are still phthalate esters, which are usually added in a content of up to 50% of the final weight of the products. When used in applications like medical devices or toys, toxic and biological effects can arise from transfer of plasticizer to humans. In December 1999, the European Commission issued an emergency ban (1999/815/EG) on the use of 6 phthalate esters in toys and childcare articles that are intended to be placed in the mouth of children under the age of three. In July 2005 the European Parliament expanded the ban forbidding the use of three of the most common phthalate esters in all toys and childcare articles within the European Union. The fate of phthalate esters in environments such as soil [7], marine ecosystem [8], and indoor air [9] has also been studied. Janjua et al [10] showed that some of the phthalate esters have the ability to penetrate human skin.

Even though several commercial alternatives have appeared they usually have not been able to match the phthalate esters as more or less “universal” plasticizers. There

is thus still need for more research to find high-performance plasticizers that are safe and environmentally friendly. We have previously during an EU-funded project: “Biocompatible flexible polymer alloys based on polyesters from renewable resources for mass-consumer applications involving contact with human fluids and tissues”, developed possible polymeric plasticizers based of different polycaprolactone copolymers. The developed PVC blends could be processed with same equipment than PVC/phthalate blends. They also had similar mechanical properties and were stable towards migration during prolonged periods in aqueous solutions [11]. We also showed the effect of macromolecular architecture on the plasticizing efficiency and migration resistance of poly(butylene adipate) based plasticizers [12,13,14]. In our latest work, we synthesized different isosorbide oligoesters based on renewable isosorbide and evaluated the obtained compounds as PVC plasticizers with promising results [15].

Many polymer additives with possible environmental and health effects are still used in huge quantities. In addition many of these compounds are synthesized from oil-based resources. The aim of the project was to recycle non-edible biomass waste to value-added products and simultaneously produce alternative plasticizers to replace the questionable phthalate plasticizers still used in most flexible PVC products. No previous work was found from the literature concerning the development of plasticizers from liquefied waste paper. However, since most existing plasticizers are different esters, there were good prerequisites that the ester deduced from liquefied biomass could be used as plasticizers for different plastic materials.

2. Experimental

2.1 Liquefaction of paper

Two types of waste paper (regular white paper (WP) and brown hand tissue paper (BP)) were liquefied to polyols by acid catalysed solvolysis in glycerol/ethylene glycol [6] (Figure 1a). The purified polyols and their chemical structures were characterized by fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR) and electrospray-ionisation mass spectrometry (ESI-MS). In addition the scanning electron microscopy (SEM) was used to evaluate the effect of liquefaction. The residues were dried in oven and used for calculation of the liquefaction ratio according to eq. 1. The liquefaction ratio was 86 % for brown paper, but only a few % for white paper.

$$\text{Liquefaction ratio} = \frac{\text{Weight of Residue (g)}}{\text{Weight of added wood powder (g)}} \quad [1]$$

2.2 Synthesis of plasticizers

The liquefaction polyol products were used as renewable resource monomers to prepare new plasticizers for PVC materials. The liquefied brown paper (LBP) was reacted with hexanoic acid with dibutyl tin oxide catalyst to synthesize ester plasticizers by a condensation reaction. After purification and precipitation the ester plasticizers were obtained and denoted as liquefied brown paper esters (LBPE) and liquefied white paper esters (LWPE) (Figure 1b). The molecular weight and chemical structure of LBP and LBPE were analyzed by size exclusion chromatography (SEC). FTIR, NMR and ESI-MS.

2.3 Preparation of PVC blends

The prepared plasticizers were blended with PVC by solution casting and tested as new generation PVC plasticizers. The solvent used was tetrahydrofuran (THF). The plasticizer concentration was 20 or 40 wt-%. In addition PVC was blended with corresponding amount of traditional phthalate plasticizer, diisooctyl phthalate (DIOP) for comparative purposes.



Figure 1. a) liquefaction of waste paper, b) purification of plasticizer.

2.4 Characterization of plasticizers and PVC/plasticizer blends

The liquefied products and synthesized plasticizers were characterized by FTIR, NMR, ESI-MS, SEC and SEM. The thermal and mechanical properties of PVC/LBPP and PVC/LWPP blends were determined by differential scanning calorimetry (DSC) and tensile testing (Instron) and compared with PVC/DIOP blends. The miscibility of the blends was evaluated by DSC and FTIR. The instruments used were Mettler-Toledo DSC 820, Instron 5566 from Bristol, Ultra-high resolution FE-SEM (Hitachi S-4800), Perkin Elmer Spectrum 2000 FTIR, fourier transform nuclear magnetic resonance spectrometer (FT-NMR), Viscotek TDA model 301 triple detector array SEC and Finnigan LCQ ion trap mass spectrometer (ESI-MS).

3. Results and discussion

Two different paper products were liquefied and the resulting polyols were used as monomers for ester plasticizer synthesis. The synthesized plasticizers were characterized and blended with PVC. The properties and plasticizing efficiency was compared with traditional plasticizer DIOP.

3.1 Mechanical properties of PVC/plasticizer blends

The mechanical properties of PVC films containing 20 wt-% or 40 wt-% of commercial DIOP plasticizer or the synthesized plasticizers (LBPP and LWPP) were evaluated by tensile testing. The results are summarized in the table 1. As seen from the table the LBPP and LWPP plasticizers show similar or even better plasticizing efficiency for PVC than the traditional plasticizer DIOP.

Table 1. Mechanical properties of the PVC/plasticizer films.

Films	Stress at Break (MPa)	Strain at Break (%)	E-Modulus (MPa)
DIOP20	29±8	181±39	1008±51
LBPP20	33±2	244±30	961±39
LWPP20	16±1	251±18	441±66
DIOP40	17±1	416±32	8±1
LBPP40	19±4	344±41	18±1
LWPP40	12±1	337±39	54±12

3.2 Blend miscibility

Miscibility between the plasticizer and PVC is crucial for the plasticizing efficiency as well as for the long-term properties of the materials. The glass transition temperature (T_g) was analyzed by differential scanning calorimetry and showed a single glass transition temperature and a decreasing T_g value with increasing plasticizer concentration indicating good miscibility between plasticizer and PVC (see Table 2). The T_g for all 20 wt-% blends was just under room temperature, while the

40 wt-% blends exhibited Tg values significantly below room temperature. This is also clearly reflected by the strain at break values in Table 1. The Tg of 40 wt-% LBPP and LWPP blends was even lower than the Tg of the films containing 40 wt-% DIOP.

Table 2. Tg values for the different PVC/plasticizer films.

Material	Glass transition Tg (°C)
DIOP20	20
LBPP20	18
LWPP20	13
DIOP40	-32
LBPP40	-54
LWPP40	-39

Further evaluation of blend miscibility was performed by FTIR as it is known that miscibility between PVC and ester plasticizers causes a shift in the wavelength of the carbonyl absorption band. FTIR spectra of PVC/DIOP and PVC/LWPP blends are shown as examples in Figure 2 and Figure 3. The carbonyl absorption band is indicated by blue circle. There is a clear wavelength shift in the absorption band both for DIOP and LWPP blends indicating, in correlation with DSC studies, good miscibility for the prepared blends.

4. Conclusions

The acid catalyzed liquefaction process worked very well for the brown paper, but no effective liquefaction of white paper was achieved. For white paper there is, thus, a need to further develop a more efficient liquefaction process. The polyols from both liquefaction processes were utilized as monomers for plasticizer synthesis. The plasticizers were blended with PVC and the blend properties and plasticizing efficiency were compared with traditional PVC/DIOP blends. This comparison showed very promising results with similar or even improved plasticizing efficiency for the new plasticizers. Further characterization of the plasticizers and blends is still under process. A manuscript is under preparation and will be submitted for publication in near future.

References

1. E. Jasiukaityte, M. Kunaver, M. Strlic, *Cellulose* 2009, 16, 393
2. S.-H. Lee, Y. Teramoto, N. Shiraishi, *J Appl Polym Sci* 2002, 83, 1473
3. S.-H. Lee, Y. Teramoto, N. Shiraishi, *J Appl Polym Sci* 2002, 83, 1482
4. S.-H. Lee, T. Ohkita, Y. Teramoto, *J Appl Polym Sci* 2005, 95, 975
5. W.-J. Lee, Y.-C. Chen, C.-C. Wu, Y.-M. Juan, *J Appl Polym Sci* 2009, 113, 1257
6. M. Kunaver, E. Jasiukaityte, N. Cuk, J.T. Guthrie, *J Appl Polym Sci* 2010, 115, 1265
7. P. Di Gennaro, E. Collina, A. Franzetti, M. Lasagni, A. Luridiana, D. Pitea, G. Bestetti, *Environ Sci Technol* 2005, 39, 325
8. C.E. Mackintosh, J.A. Maldonado, M.G. Ikonou, F. Gobas, *Environ Sci Technol* 2006, 40, 3481
9. P.A. Clausen, V. Hansen, L. Gunnarsen, A. Afshari, P. Wolkoff, *Environ Sci Technol* 2004, 38, 2531
10. N.R. Janjua, G.K. Mortensen, A.M. Andersson, B. Kongshoj, N.E. Skakkebaek, H.C. Wulf, *Environ Sci Technol* 2007, 41, 5564
11. M. Hakkarainen, *Polym Degrad Stab* 2003, 80, 451
12. A. Lindström, M. Hakkarainen, *J Appl Polym Sci*, 2006, 100, 2180
13. A. Lindström, M. Hakkarainen, *J Appl Polym Sci* 2007, 104, 2458
14. A. Lindström, M. Hakkarainen, *Biomacromolecules* 2007, 8, 1187
15. B. Yin, M. Hakkarainen, *J Appl Polym Sci* 2011, 119, 2400.