

THE USE OF ESTERIFIED LIGNIN FOR SYNTHESIS OF DURABLE COMPOSITES

Olsson, S.,¹ Östmark, E.,^{1,2} Ibach, R.E.,³ Clemons, C.M.,³ Segerholm, K.B.,^{1,4} & Englund, F.¹

ABSTRACT

Lignin is a natural polymer and one of the most abundant materials on earth. Despite this fact, lignin is often viewed as a by-product in chemical pulp processing and the use of lignin as a sustainable material is low. However, research and public awareness of sustainability have opened up new possibilities for using lignin as a material.

In this study, Kraft softwood lignin was reacted with acetic and propionic anhydride to synthesize esterified lignin. Reactions were performed at 80 °C. The product was analyzed using IR, DSC and processability parameters, such as melt viscosity. The product was then blended with LDPE and extruded into composite films. The films were analyzed using FTIR and TGA, and the mechanical properties were determined by tensile tests. Preliminary results are positive and further studies are planned to confirm the results and establish the range of properties attainable.

Key words: Modified lignin, LDPE, WPC, compatibility.

INTRODUCTION

Lignin is a natural polymer which together with hemicelluloses performs as a matrix material bonding cellulosic fibers together, in order to give strength to the plant cell wall. Considering the fact that it is the second most abundant organic compound on earth, lignin is without doubt an underutilized resource (Fox and McDonald 2005). It is often viewed as a mere by-product from chemical pulp processing and is mainly used for energy generation. However, research and public awareness of sustainable materials have created new opportunities for using lignin. One drawback of using lignin is its low compatibility with common plastics, such as LDPE, but by introducing new functional groups this could be overcome. One method of tailoring lignin into a usable thermoplastic for composites, could be to modify the lignin polymer by esterification. This could reduce the volumes of petroleum based plastics used today and would also introduce a biomaterial to be used in a number of plastic products.

¹ SP Technical Research Institute of Sweden, SP Trätekt/EcoBuild, P.O. Box 5609, Drottning Kristinas väg 67, SE-114 86, Stockholm, Sweden,

² KTH Royal Institute of Technology, div. of Fibre and Polymer Technology

³ USDA FS Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53726, USA

⁴ KTH Royal Institute of Technology, div. of Building Materials

MATERIAL AND METHODS

Synthesis and production of sample films

In this study, kraft softwood lignin (KSL), kindly supplied by Innventia, was reacted with acetic and propionic anhydride to synthesize esterified lignin (LAP). During the first part of the study, smaller batches using 10 g of KSL, 100 mmol of acetic anhydride and 300 mmol of propionic anhydride, were synthesized. The reactions were performed at 80 °C and 100 °C, in order to determine any temperature effects. For the second part of the study, the reaction performed at 80 °C was upscaled to 100 g of KSL with a corresponding increase of anhydride. The reaction procedure was similar to previously reported ones (Steward et al. 2002). The product was analyzed using FTIR, optical microscopy and processability parameters. The product from the larger batch was then blended with LDPE and compounded into composites using different processing temperatures.

All films were produced by compounding and film extrusion on a DSM Xplore, 15 ml micro compounder / extruder into 30 mm wide films. The dry weight ratio of the LAP was kept constant at 10% for all the samples. Four composite samples were prepared, the first three samples were prepared by dry blending 11 g, compounding and extruding films, the screw speed was kept constant at 50 rpm, the temperature was 150, 160 and 170 °C for the three first samples. The fourth sample was prepared by pre-compounding an 8g, 50/50 mix of LAP and LDPE with a screw speed of 150 rpm and 150 °C. The compound was then dry blended with LDPE to get an 11g blend with 10% LAP followed by compounding and film extruding at the same speed as the first three samples at a temperature of 150 °C (Preblend 150 °C). As a reference, pure LDPE was extruded at 160 °C.

Physiochemical Characterization

Attenuated Total Reflection-Fourier Transform Infrared Spectroscopy (ATR-FTIR) was used and all measurements were performed in air at room temperature. The equipment used was a Perkin-Elmer Spectrum 2000 FT-IR equipped with a MKII Golden Gate, Single Reflection ATR System from Specac Ltd., London, U.K. The ATR crystal was a MKII heated Diamond 45° ATR Top Plate.

Thermogravimetric analysis (TGA) was used to study the thermal properties of the films. The equipment used was a Mettler Toledo thermogravimetric analyser with a sample robot, and all samples were heated from 25 to 600 °C in air.

Differential Scanning Calorimetry (DSC) was used to analyze the thermal properties of the films. The analyses were performed on a DSC 820 equipped with a sample robot and a cryocooler (Mettler Toledo). The DSC runs were carried out in closed sample pans sealed in air using the following temperature program: heating from 25 to 160 °C (or 300 °C) at 50 °C/min, followed by cooling from 160 °C (or 300 °C) to -20 °C at -50 °C/min and then a final heating to 180 °C (or 300 °C). Before and after cooling the samples were kept isothermally for 10 and 5 minutes respectively.

For the optical microscopic images, an Olympus BX51 was used and the samples were pressed together by glass microscope slides.

Tensile tests were performed on dumbbell shaped samples from all the extruded films at a pulling speed of 10 mm/minute. The width of all samples was 0.3175 mm with a thickness ranging from approximately 0.13 to 0.45 mm.

RESULT AND DISCUSSION

Initially, the produced films were visually assessed and it was concluded that the process temperature does affect the final film (Fig. 1). A starting temperature of 160°C lead to a brown colored film, indicating well-distributed LAP in the LDPE, and an increase in temperature to 170°C resulted in a highly separated film, with small islands of aggregated LAP in the LDPE matrix. However, a decrease in temperature and pre-blending of the two components resulted in an improvement of the produced films, which was also supported by the microscopic images (Fig. 2).



Fig. 6 Photograph of films. From left: Pure LDPE, LAP 150°C, LAP 160°C, LAP 170°C and LAP 150°C pre-blend.

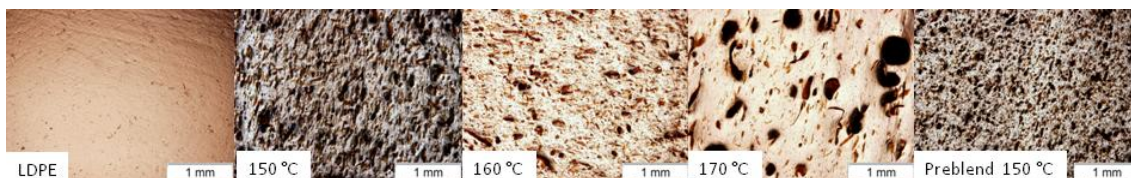


Fig. 7 Microscopic images of the produced films.

By studying the FTIR spectra (Fig. 3) of the unmodified and the esterified lignin (LAP) it was confirmed that the reactions had occurred since some large differences could be seen in the spectra. One of the most obvious differences was the major decrease in the peak at approximately 3000-3600 cm^{-1} , representing the phenolic and aliphatic hydroxyl groups. Another difference is the large increase of the carbonyl peak at *ca* 1730 cm^{-1} , which originates from the esters formed when the anhydrides react with lignin hydroxyl groups. Both of these differences are in accordance with previous studies (Steward et al. 2002, Glasser and Jain 1993).

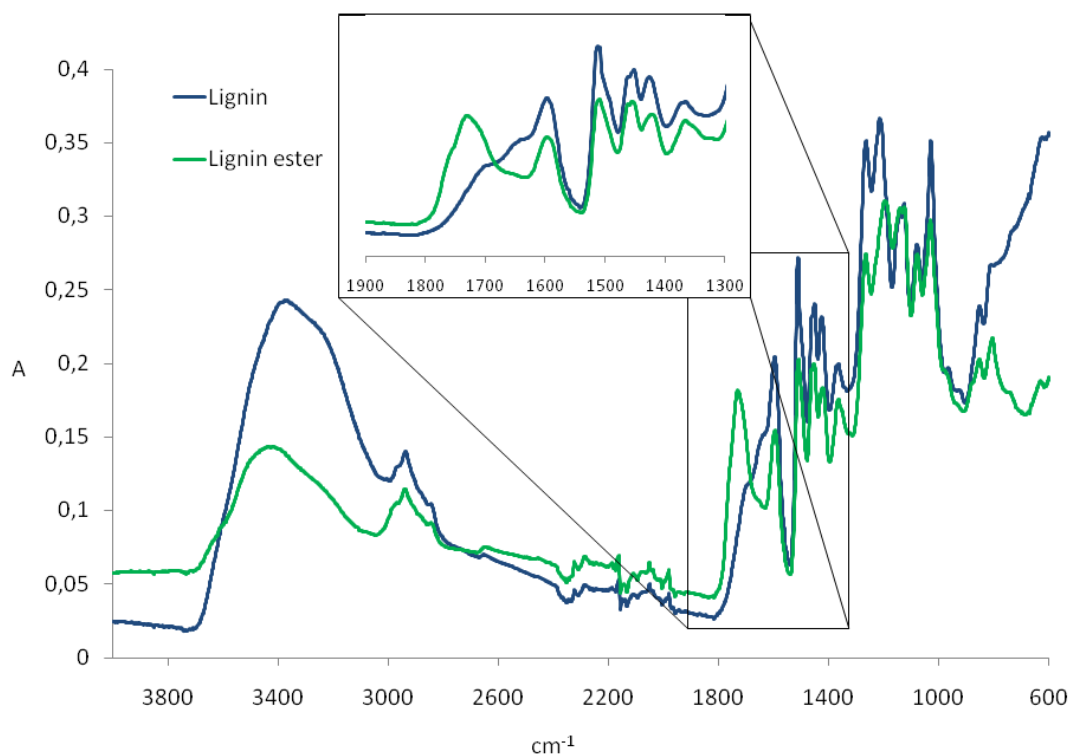


Fig. 8 FTIR spectra of lignin (black line) and modified lignin (grey line). The zoomed insertion shows the region of 1900-1300 cm^{-1} .

The DSC results (Fig. 4) show a clear melting point (T_m) for LDPE at 110-120°C. However, the effect of the lignin on the T_m appears to be very low, and the DSC curves still exhibit a high level of crystallinity, indicating that the miscibility is not that good.

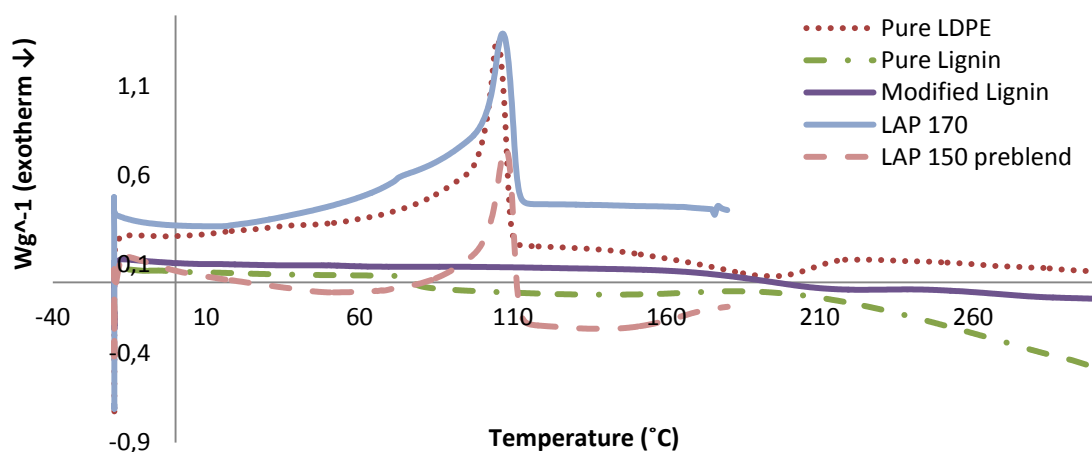


Fig. 9 DSC thermograms (2nd heating scan) for lignin, LDPE and two of the four LAPs.

Fig. 5 show the results from the TGA measurements, and by comparing the thermograms for lignin and modified lignin it can be concluded that esterification of the lignin affects the thermal stability of the material. The results also show that the final degradation temperature of the lignin is somewhat increased when modified with anhydride. The curves representing pure LDPE and LAP indicate that adding lignin

could possibly decrease the amount of oxidation during degradation, which in turn increases the thermal stability.

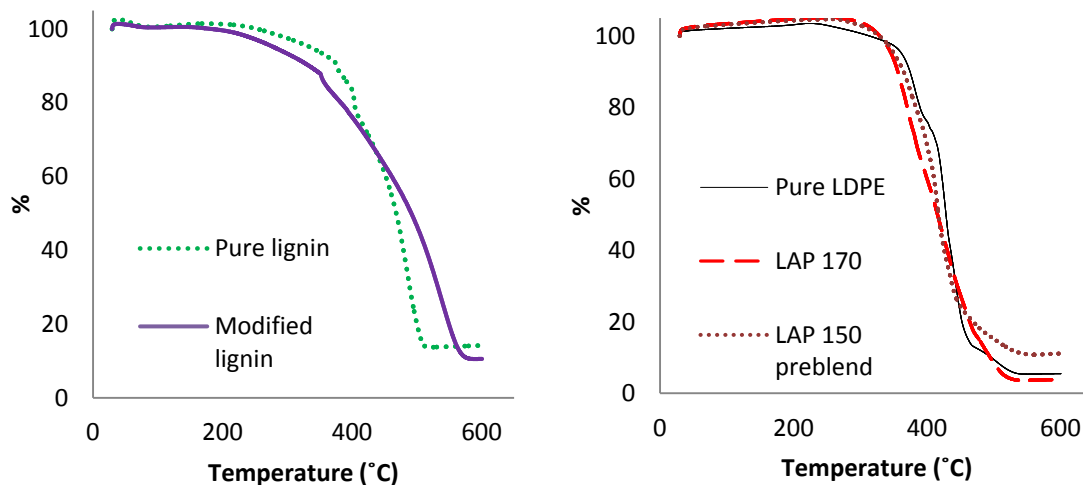


Fig. 10 TGA thermograms for lignin, LDPE and two of the four LAPs.

Results from the tensile testing shows decreased strength for all composite samples compared to the pure LDPE, the 170 °C sample show lower stress at break which is most likely related to large LAP aggregates formed within the composite at this temperature. The stiffness is also lower for the 150 °C, 160 °C and pre-blend 150 °C samples, whereas the 170 °C samples show increased stiffness due to the large aggregates of LAP in the LDPE matrix.

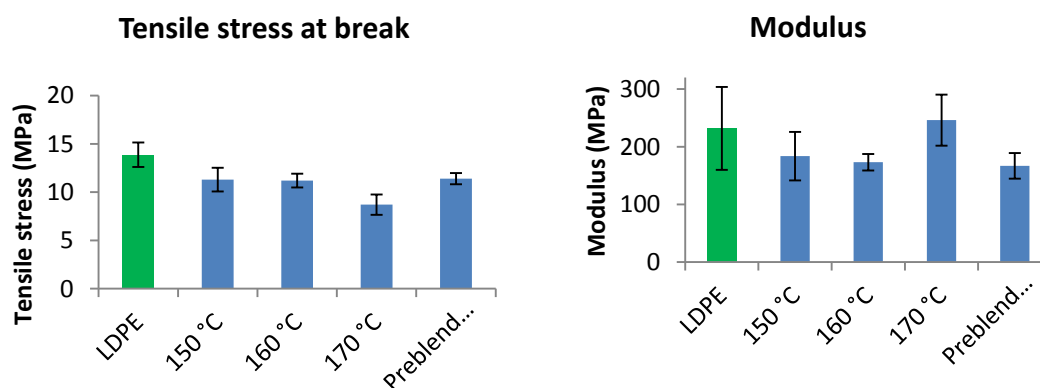


Fig. 11 The graphs illustrate tensile stress at break and modulus for a pure LDPE film in comparison to the four different LAP-LDPE composites.

CONCLUDING REMARKS

- The FTIR spectra show that esterification of lignin is possible
- The LAP used did not blend well with the LDPE and is in this case to be considered as a filler material
- At 170 °C processing temperature the LAP formed larger aggregates which caused uneven films and crack initiations when mechanically tested

FUTURE WORK

Future work of interest is to use modified lignin that has been esterified at 100 °C instead of 80 °C. The first part of this study indicates that increasing the temperature results in higher degree of acetylation which in turn could increase the compatibility with LDPE.

Another interesting aspect would be to vary the molar ratio between the two anhydrides, and also to use the anhydrides separately.

ACKNOWLEDGEMENTS

Thanks to Innventia for providing kraft softwood lignin and to Nicklas Kloo, SP Trätek, for microscopy imaging.

REFERENCES

Fox, S.C. & McDonald, A.G. 2005. The esterification of different industrial lignins to form lignin bioplastics. Proceedings from the 37th SAMPE Fall Technical Conference. Seattle, USA.

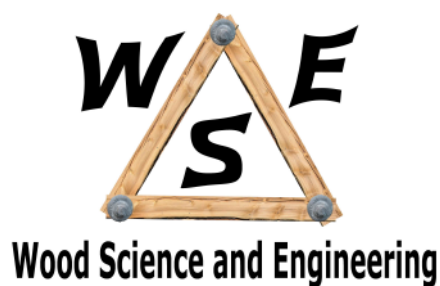
Glasser, W.G. & Jain, R.K. 1993. Lignin Derivatives. I. Alkanoates. *Holzforschung* 47: 225-233.

Steward, D., McDonald, A.G. & Meder, R. 2002. Thermoplastic lignin esters. Proceedings from the 6th Pacific Rim Bio-Based Composites Symposium. Portland, USA. p. 584-594.

Proceedings of the 7th meeting of the
**NORDIC-BALTIC NETWORK IN WOOD
MATERIAL SCIENCE & ENGINEERING
(WSE)**

October 27-28, 2011, Oslo, Norway

Edited by Erik Larnøy and Gry Alfredsen



ISBN: 978-82-311-0139-0

ISSN: 1891-7933

Cover Photo: Spiral pattern of reaction wood in spruce. Photo: Andreas Treu, Skog og landskap

Norsk institutt for skog og landskap, Pb. 115, NO-1431 Ås