Technical University of Denmark

Thermal transitions of the amorphous polymers in wheat straw

Stelte, Wolfgang; Clemons, Craig; Holm, Jens K.; Ahrenfeldt, Jesper; Henriksen, Ulrik Birk; Sanadi, Anand R.

Published in:
Industrial Crops and Products

Link to article, DOI:
10.1016/j.indcrop.2011.03.014

Publication date:
2011

Thermal transitions of the amorphous polymers in wheat straw

Wolfgang Stelte [a], Craig Clemons [b], Jens K. Holm [c], Jesper Ahrenfeldt [a], Ulrik B. Henriksen [a] and Anand R. Sanadi [d]*

[a] Biosystems Department, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark.

[b] Forest Products Laboratory, United States Department of Agriculture, 1 Gifford Pinchot Dr., Madison 53726-2398, WI, USA.

[c] DONG Energy Power A/S, A.C. Meyers Vænge 9, DK-2450, Copenhagen SV, Denmark.

[d] Forest & Landscape Denmark, Faculty of Life Sciences, University of Copenhagen, Rolighedsvej 23, DK-1985 Frederiksberg C, Denmark.

The thermal transitions of the amorphous polymers in wheat straw were investigated using dynamic mechanical thermal analysis (DMTA). The study included both natural and solvent extracted wheat straw, in moist (8-9 % water content) and dry conditions, and was compared to spruce samples. Under these conditions two transitions arising from the glass transition of lignin and hemicelluloses have been identified. Key transitions attributed to softening of lignin were found at 53, 63 and 91 °C for moist wheat straw, extracted straw and spruce, respectively. Transitions for hemicelluloses were determined at 2, -1 and 5 °C respectively. Differences are likely due to different compositions of lignin and hemicelluloses from straw and spruce and structural differences between the raw materials. The high wax content in wheat straw resulted in a transition at about 40 °C which was absent in solvent extracted wheat straw samples and spruce. This specific transition was further investigated and confirmed by differential scanning calorimetry (DSC) of extracted wheat straw wax. Information

*) Corresponding author. E-mail: wost@risoe.dtu.dk; Tel.: +45 2132 5175; Fax: +45 4677 4109

about the thermal transitions is of great importance for the utilization of wheat straw in pelletizing, briquetting and fiber board manufacturing.

Key words: wheat straw, thermal transitions, DMTA, lignin, hemicelluloses, glass transition temperature, DSC

1. Introduction

Wheat is one of the most grown crop species in the world and its annual production is estimated to be about 650 million tons per year (Atwell, 2001). Wheat straw is increasingly being used as a source for renewable energy, and is either fired directly or upgraded to higher energy density by means of pelletization or briquetting (Olsson, 2006). It is also used in the production of medium density fiber boards, MDF (Halvarsson et al., 2010). Deswarte et al. (2007) have recently presented an integrated straw based bio-refinery concept where the utilization of straw components, i.e. the wax and the fiber fraction, and their transfer into high value products are described in detail.

Wheat straw, like wood, can be considered as a composite material, and its mechanical properties are determined by the interactions between its individual polymers. Lignin and hemicelluloses are essentially amorphous polymers, while cellulose has both amorphous and crystalline regions (Fengel and Wegner, 1983). For amorphous polymers, the softening or glass transition (T_g), is one of the major parameters influencing its viscoelastic properties. Above this temperature, the mobility of the polymer backbone (e.g. rotation around its own axis) increases, resulting in a drop of storage modulus and a further transition from a glassy into a rubbery state (Grellmann and Seidler, 2005). The moisture content is an important factor affecting the viscoelastic properties of lignin and hemicelluloses. Water acts as a plasticizer, causing a reduction of the energy required to initiate chain mobility (Kelley et al., 1987).

Dynamic mechanical thermal analysis (DMTA) is a tool widely used in material science to study the relaxation behavior of polymers (Grellmann and Seidler, 2005). In DMTA spectra of amorphous polymers the peaks occurring at the highest temperatures are usually labeled as α-transitions and correspond to the glass transition of the polymer backbone. The temperature of a polymer's α-transition depends on its chemical structure. In general it is found that its temperature increases depending on the stiffness of the main chain (polymer backbone) and the presence of polar and/or bulky side chains, and is reduced in case of large, flexible ones (Young and Lovell, 1991). The α-transitions found in the DMTA spectra of wood, which is like wheat straw a composite material composed out of cellulose, hemicelluloses and lignin, vary with moisture content and species (Kelley et al., 1987). Olsson and Salmen (1997) have determined that the α_1-transitions observed in the DMTA spectra of wood is the T_g of lignin and have shown how the presence or absence of certain side chains (methoxy groups) affect the T_g.

To the best of the authors' knowledge no data has been published about these transitions for wheat straw. In the present study we measured the thermal transitions of wheat straw using DMTA. Since the thermal transitions of wood and its components have been thoroughly investigated (Irvine 1984; Kelley et al., 1987; Salmen and Olsson, 1998; Sun et al., 2007), it is useful to compare those of straw with those of wood. To study, whether the high wax content found in wheat straw has an effect on the transitions, solvent extracted straw was investigated as well. The thermal transitions of the extracted wax have been studied by means of differential scanning calorimetry (DSC). Knowledge about the thermal transition of the amorphous components of wheat straw is important for the production of fuel pellets, briquettes, fiber boards and new materials that have high fiber contents (Sanadi and Caulfield, 2008). This will help to improve properties, and also help in process design for the manufacturing of these products.

2. Materials and Methods

The raw materials used in this study were wheat straw (*Triticum aestivum L.*) from local Danish farmers and Norway spruce (*Picea abies K.)* with a particle size of 1 to 3 mm. Wax was extracted from wheat straw by Soxhlet extraction in hexane for 8 hours (boiling point of hexane is about 70 °C), and then recovered from the solvent by vacuum evaporation and kept for further analysis. All materials were conditioned at 65 % RH and 27 °C for at least one week. 10 g of the conditioned materials were formed in a round mat (75.9 mm in diameter and 1.5 mm thick) by pressing it between two steel cauls at 154 °C and 50 MPa for 5 minutes using a laboratory-scale hot press. It has to be noted that hot pressing is not expected to affect the thermal transition behavior since the transitions in this study are only related to glass transition.

Rectangular specimens (17.5 mm length x 12 mm width) were cut using a utility knife. The thickness of each specimen ranged from 2.1 to 2.3 mm. The pressed specimen were conditioned in a climate chamber at 65 % RH and 27 °C for at least one week, which resulted in a moisture content of 8.4 % for straw, 8.3 % for the extracted straw and 9.0 % for the spruce. Moisture content was calculated based on weight loss after drying about 2 g sample material for 12 hours at 105 °C. The viscoeleastic properties were tested by means of DMTA (Q800, TA-Instruments, New Castle, DE, USA) using a single cantilever grip. The viscoelastic region (strain directly proportional to stress) was determined by performing a strain sweep. Specimens were removed from the climate chamber, measured in their exact dimensions and immediately fixed in the grip and cooled to -60 °C using liquid nitrogen. To obtain dry samples, the specimens were mounted in the DMTA and then heated to 150 °C and held at this temperature for 10 minutes, to ensure that the sample was as dry as possible as suggested by Sun et al. (2007). The samples were subsequently cooled to -60 °C using liquid nitrogen. Measurements were conducted between -60 and 200 °C with an amplitude of 15 µm at a frequency of 1 Hz. The storage modulus (E') and loss factor ($\tan\ \delta$) were used to determine the transitions of the amorphous polymers. A minimum of two samples were tested and data from the first run was used when it was shown to be in accordance with the second run. The average value was not calculated since small differences in moisture content (< 0.15 %) occurred that could have affected the transition temperatures.

For a more detailed study of the transition temperature of wheat straw was, the wax sample was dried in vacuum at 60 °C, and 5 mg were pressed into an aluminum capsule and tested in a DSC (DSC7, Perkin Elmer, Waltham, MA, USA). The test was run between -20 and 100 °C with a heating rate of 10 °C/min. Data acquired during the second heating cycle was used for interpretation, to ensure that good contact was made between the sample pan and the wax and to remove the previous heat history due to Soxhlet extraction, for example. The test was run for two times and results have been shown to be reproducible.

3. Results and Discussion

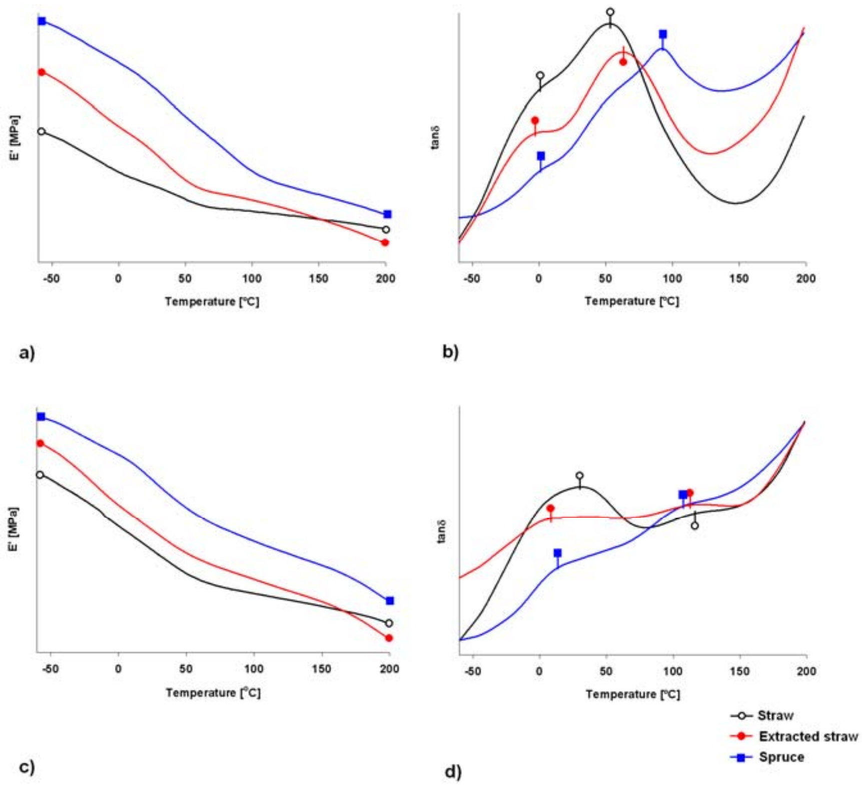

Figure 1. (a) Storage modulus (*E'*) and (b) loss factor (*tan δ*) of straw, extracted straw and spruce. The samples moisture content were 8.4 %, 8.3 % and 9.0 % for straw, extracted straw and spruce. c) Storage modulus (*E'*) and (d) loss factor (*tan δ*) of dry straw, dry extracted straw and dry spruce. It has to be noted that the scale on the y-axes (*E'* and *tan δ*) was adjusted for better comparison of the samples.

The DMTA spectra of moist straw, moist extracted straw and moist spruce (Figures 1a and 1b) have several features in common but reveal also some important differences. *E'* (Figure 1a) decreases substantially over the range of the α transitions, implying large-scale segmental movement, characteristic of polymeric glass transitions (Grellmann and Seidler, 2005). The *tan δ* responses (Figure 1b) reveal two major transitions for all samples. There is a broad α-transition (α_1) peaking at about 53 °C (straw), 63 °C (extracted straw) and 91 °C (spruce). This transition is most likely linked to the glass transition of lignin. Work by Olsson and Salmen (1997) has shown that the α_1-transition of moist wood usually occurs between 60-95 °C and is due to be the glass transition of lignin. The second major relaxation (α_2) can be found at 2 °C in case of straw and -1 °C and 5°C in case of extracted straw and spruce. The T_g of hemicelluloses in moist wood was shown to be about room temperature (Kelley et al., 1987). Therefore it is likely that the observed transitions are due to the glass transitions of hemicelluloses.

The α_1 transition of wheat straw occurs at a lower temperature than for spruce (*tan δ* peak at 55 °C compared to 95 °C). This could be due to chemical differences between their lignins. Lignins can be classified into three major groups, based on the chemical structure of their monomer units, which are: softwood lignin, hardwood lignin and grass lignin (Sun, 2010). Depending on its composition of guaiacyl (G), syringyl (S) and p-hydroxyphenylpropane (H) units, straw lignin is classified as a GSH lignin, while those of softwoods (such as spruce) are classified as G lignin and GS in case of hardwoods. Unlike straw lignin, spruce lignin does not contain syringyl and p-hydroxyphenylpropane units which might affect its T_g. Olsson and Salmen (1992) compared lignins from hardwoods and softwoods and found that softwood lignin has a higher T_g than hardwood lignin. They suggested that there are more cross-links in softwood lignin than in hardwood lignin, due to the absence of methoxy groups, increasing its T_g. It is known that lignins in wheat straw (grass) are frequently cross-linked to (mainly xylan) hemicelluloses via phenolic ester moieties which does not occur as frequently or in the same ways as in softwood (Lu and Ralph, 2010). It is also possible that naturally occurring, physical and chemical differences between wood and straw attribute to this phenomenon. Within this study the material was used in form of particles between 1-3 mm, pressed into bars of same dimensions to minimize the raw materials physical differences. Nevertheless further studies are necessary to find out what exactly causes these differences.

There is also a difference between the straw and the extracted straw (*tan δ* peak at 55 °C and 63 °C). This could be due to the wax, whose transition likely overlaps with the lower part of the lignin transition. Furthermore it might be possible that the solvent itself might have induced structural and/or compositional changes in the straw, beyond what is expected from the removal of waxes. This last phenomenon is complex and warrants further studies.

The thermo-mechanical properties of dry wheat straw, dry extracted straw and dry spruce are shown in Figures 1c and 1d. The *E'* spectra (Figure 1c) are similar for all three materials. As temperature is increased, *E'* decreases rapidly for all materials up to about 50 °C and then continues to decrease at a lower rate afterwards. Differences in the *tan δ* responses (Figure 1d) are clear. The broad transitions of that peak at about 110-120 °C, as well as the transitions around 10-20 °C, are of low intensity and might be attributed to lignin secondary transitions, found by others performing DMTA on dry wood (Hatakeyama and Hatakeyama, 2010; Sugiyama et al., 1998; Sun et al., 2007). However the straw sample exhibits a broad and intense transition at about 40 °C, which is not present in case of the extracted straw and the spruce. Therefore it is likely due to the wax, which comprises for about 4 % of the straw's dry matter (Stelte et al., 2011).

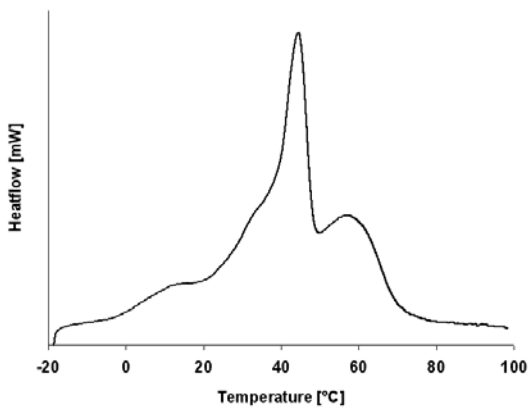

Figure 2. Thermal transitions of wheat straw wax determined by DSC.

Results from the DSC analysis of the extracted wax support this. The heating curve (Figure 2) shows a sharp endothermic peak at about 45 °C. Wax is a hydrophobic substance and it's T_g is unlikely to be affected by the moisture content of the straw sample. Therefore it is likely that the transition of wax in the moist sample (Figure 1b) was covered under the intense transitions of the hemicelluloses. The softening and the subsequent flow of the waxes at low temperatures is problematic since it has been shown to inhibit adhesion between straw particles in fuel pellet production, resulting in the formation of weak boundary layers that are responsible for the low compression strength of straw pellets compared to wood pellets (Stelte et al., 2011). Another interesting feature is that the E' of moist extracted straw (Figure 1a) shows a drop at about 130 °C and at about 160 °C under dry conditions (Figure 1c) which is not seen in raw wheat straw. This suggests that in case of the extracted straw, lignin flows at lower temperature and could result in improved mechanical properties of products made out of compressed straw.

4. Conclusion

The results show that wheat straw possesses similar thermal transitions as spruce and that the transitions are affected by the presence of moisture in these materials. The α transitions of moist wheat straw (8.4 % water content) take place at 2 °C and 53°C and are contributed to the glass transition of hemicelluloses and lignin, respectively. For spruce (9 % water content) slightly higher transition temperatures of 5 °C and 91 °C were found. This difference is likely contributed by a different chemical composition of the lignin and probably morphological and structural differences between wheat straw and spruce. Information about the transitions and thus the T_g is of great importance for the utilization of wheat straw in pelletizing, briquetting and fiber board manufacturing processes since a flow of the amorphous polymers is a requirement for the formation of strong inter particle bonding by solid bridge formation between adjacent particles.

Acknowledgements

The present study was conducted under the framework of the Danish Energy Agency's EFP project: "Advanced understanding of biomass pelletization" ENS-33033-0227. The authors wish to thank Vattenfall AB, DONG Energy A/S and the Danish Energy Agency for funding. The USDA - Forest Products Laboratory in Madison, Wisconsin is thanked for its hospitality and the provision of laboratory space and equipment for this study.

References

Atwell, W.A., 2001. An overview of wheat development, cultivation, and production. Cereal Food World, 46(2), 59-62.

Deswarte, F.E.I., Clark, J.H., Wilson, A.J., Hardy, J.J.E., Marriott, R., Chahal, S.P., Jackson, C., Heslop, G., Birkett, M., Bruce, T.J., Whiteley, G., 2007. Toward an integrated straw-based biorefinery. Biofuels Bioproducts, 1(4), 245-254.

Fengel, D., Wegner, G., 1983. Wood - chemistry, ultrastructure, reactions. Kessel Verlag, Remagen.

Grellmann, W., Seidler, S., 2005. Kunststoffprüfung. Carl Hanser Verlag, München.

Halvarsson, S., Edlund, H., Norgren, M., 2010. Wheat straw as raw material for manufacture of medium density fiberboard (MDF). Bioresources, 5(2), 1215-1231.

Hatakeyama, H., Hatakeyama, T., 2010. Thermal properties of isolated and in situ lignin. In: Heitner, C., Dimmel, D., Schmidt, J. (Eds.) Lignin and Lignans: Advances in Chemistry, CRC Press. New York, pp. 301-316.

Irvine, G.M., 1984., The glass transitions of lignin and hemicellulose and their measurement by differential thermal-analysis. Tappi, 67(5), 118-121.

Kelley, S.S., Rials, T.G., Glasser, W.G., 1987. Relaxation behavior of the amorphous components of wood. J. Mater. Sci., 22(2), 617-624.

Lu, F., Ralph, J., 2010. Lignin. In: Sun, R.C. (Ed.) Cereal straw as a resource for sustainable biomaterials and biofuels. Elsevier, Amsterdam, pp. 169-207.

Olsson, A.M., Salmen, L., 1992. Viscoelasticity of insitu lignin as affected by structure - softwood vs hardwood. Viscoelasticity Biomaterials, 489, 133-143.

Olsson, A.M., Salmen, L., 1997. The effect of lignin comosition on viscoelatsic properties of wood. Nordic Pulp Paper Res., 12(3), 140-144.

Olsson, M., 2006. Wheat straw and peat for fuel pellets - organic compounds from combustion. Biomass Bioenergy, 30(6), 555-564.

Salmen, L., Olsson, A.M., 1998. Interaction between hemicelluloses, lignin and cellulose: Structure-property relationships. J. Pulp Pap. Sci., 24(3), 99-103.

Sanadi, A.R., Caulfield, D., 2008. Thermoplastic Polyolefins as Formaldehyde Free Binders in Highly Filled Lignocellulosic Panel Boards: Using Glycerine as a Processing Aid in Kenaf Fiber Polypropylene Boards. Mat. Res., 11(4), 487-492.

Stelte, W., Holm, J.K., Sanadi, A.R., Barsberg, S., Ahrenfeldt, J., Henriksen, U.B., 2011. A study of bonding and failure mechanisms in fuel pellets from different biomass resources. Biomass Bioenergy, 35, 910-918.

Sugiyama, M., Obataya, E., Norimoto, M., 1998. Viscoelastic properties of the matrix substance of chemically treated wood. J. Mat. Sci., 33(14), 3505-3510.

Sun, N., Das, S., Frazier, C.E., 2007. Dynamic mechanical analysis of dry wood: Linear viscoelastic response region and effects of minor moisture changes. Holzforschung, 61(1), 28-33.

Sun, R., 2010. Cereal straw as a resource for sustainable biomaterials and biofuels: chemistry, extractives, lignin, hemicelluloses and cellulose. Elsevier, Amsterdam.

Young, R.J., Lovell, P.A., 1991. Introduction to polymers - 2nd edition. CRC Press, Boca Raton.