Preliminary Studies on Converting Agricultural Waste into Biodegradable Plastics – Part III: Sawdust

Christopher H. Schilling,[1,4] Piotr Tomasik,[2] David S. Karpovich,[3] Bruce Hart,[1] Jagdeep Garcha,[1] and Paul T. Boettcher[1]

Hardwood sawdust was derivatized either by carboxymethylation, glutaration, maleiation, phthallation, or succination in order to produce anionic materials suitable for complexation with soy protein isolate. Blending each derivative with soy protein isolate resulted in instant precipitation of gels. Infrared spectroscopy and differential scanning calorimetry suggested that each derivative formed a complex with protein. Reaction products could be dried into pellets exhibiting tensile strengths between 0.9–2.4 MPa, suggested that these materials could be promising candidates for biodegradable structural materials.

KEY WORDS: Anionic polysaccharides; cellulose; lignin; polysaccharide – protein complexes; wood.

INTRODUCTION

This paper is third in a series of four papers on the synthesis of protein—anionic polysaccharide compounds that appear to have promise as biodegradable structural materials. [1–3]. Our intent is to produce these materials from simple, aqueous, economical, and environmentally-safe methods that rely on abundant, low cost biomass feedstocks usually considered by-products or waste products from agricultural or industrial sources. Having the look and feel of wood or hard plastics, these materials have potential applications that include furniture, architectural panels, temporary landscaping structures, and fugitive patterns to replace wood and polystyrene foam in composite molding applications. This paper focuses on the use of sawdust as an abundantly-available polysaccharide waste material as feedstock. The remaining three papers focus on feedstocks of corn distillers' dry grain [1, 3], corncobs [2, 3], and sugar beet pulp [3].

Six primary factors motivate this research: (1) the continuously accelerating consumer use and landfill disposal of traditional plastics; (2) the accelerating costs of landfilling; (3) satisfactory landfill sites are becoming scarce, and alternative disposal methods are becoming limited; (4) the fact that traditional plastics are made from petroleum, a non renewable, imported resource that is becoming limited in global supply; (4) the fact that petroleum-derived plastics biodegrade slowly and persist for many years after landfilling; and (6) although a growing number of manufacturers produce biodegradable, agriculturally-derived polymers, these materials tend to be costly because they rely on sophisticated chemical processing (e.g., distillation, microbial fermentation). The first paper in this series reviews each of these factors in greater detail [1]. Several authors provide excellent, comprehensive reviews of this background information [4–7].

[1] Department of Mechanical Engineering, Saginaw Valley State University, 7400 Bay Road, University Center, MI 48710, USA.
[2] Department of Chemistry, University of Agriculture, Cracow, Poland.
[3] Department of Chemistry, Saginaw Valley State University, University Center, MI 48710, USA.
[4] To whom all correspondence should be addressed. E-mail: schillin@svsu.edu

Upon consideration of factors (1) to (6) above, it is clear that technological breakthroughs are needed to make altogether new types of biodegradable materials from less expensive chemical processes. Ideally, these new processes would rely on cheap and abundant biomass feedstocks that are considered by-products or waste products from industrial sources. In order to address this problem, several researchers have conducted laboratory experiments to produce biodegradable solids from inexpensive polysaccharide residues including wood cellulose, hemi cellulose from straw, grass, leaves, fruits and vegetables, and starch from cereals and tubers [8–22]. Other researchers demonstrated the feasibility of making biodegradable plastics either from soy protein or from complexes of proteins with polysaccharides [23–30].

Protein complexation with polysaccharides requires the latter to be anionic [31, 32]. There are several papers published on complexes of protein with anionic polysaccharides including potato starch [33–35], pectins [36–38], carageenans [39, 40], xanthan gum [41, 42] and carboxymethylcellulose [43–45]. It has been proven that interactions between proteins and those anionic polysaccharides involved mainly electrostatic interactions but also random covalent bonding between proteins and polysaccharides. In another two papers, milk casein was complexed with either potato starch [46] or cornstarch [Nagenauer et al., *Molecules,* submitted.] ionized by phosphation. The same type of electrostatic and covalent interactions was proven in those papers, and the biodegradability of resulting complexes was also demonstrated. In this paper, we anionized sawdust either by carboxymethylation, glutaration, maleiation, phthallation or succination in order to produce anionic materials suitable for complexation with soy protein isolate.

We chose sawdust as a raw material for this process, because lignocellulosic wastes are in abundant supply. For example, the U.S. currently generates 120 billion pounds of paper mill waste and 75 billion pounds of urban tree residue annually [4]. Several value-added applications of sawdust have been reported in the literature including charcoal [47] and solid fuel consisting of pelleted or briquetted sawdust [48–50]. Co-fermentation of sawdust with manure [51] and co-liquefaction with coal [52] are alternative routes to energy production. The sorptive properties of sawdust have resulted in its application as a collector of heavy metals and other toxins from wastewater and soil [54–55]. In addition, the use of sawdust as construction material for wood product boards and panels has been known since the nineteenth century. Recent developments include the use of sawdust for reinforcing polymers [56, 57] and as a component of wood-based cement-bonded boards [58].

Wood is a complex material composed of the polysaccharide, cellulose, along with 16–32% lignin, which is a polyphenol carrying the phenol, enol, carboxyl, and the primary and secondary alcohol hydroxyl groups [59]. Thus, both major components of wood can be acylated becoming anionic. Lignin is naturally anionic. Given the high concentration of cellulose in sawdust, it is likely that sawdust can be derivatized by reaction with cyclic anhydrides or chlorocarboxylic acids. Such derivatization anionizes the polysaccharides present in sawdust, which in turn promotes the formation of a solid reaction product with protein [1, 31]. The resulting complexes form hard solids that appear to be viable as biodegradable structural materials. Previously, we had shown the success of this approach in the case of corn distillers' dry grain [1] and corncobs [2].

EXPERIMENTAL

Materials

Sawdust in the form of hardwood chips was provided by Putt, Incorporated (Freeland, Michigan, U.S.A.). These chips were pulverized in a kitchen blender and subsequently size fractionated using a series of sieve screens. The fine fraction, which passed through a 30 mesh screen, was used in subsequent derivatization.

The following reagent grade chemicals were purchased from the manufacturer: glutaric, maleic, phthallic, and succinic anhydrides as well as sodium chloroacetate (Aldrich, Milwaukee, Wisconsin, U.S.A.).

Soy protein isolate (066-974, PRO-FAM 974) was provided by the manufacturer (Protein Specialties Division, Archer Daniels Midland Company, Decatur, Illinois, U.S.A.) and contained 6 % moisture, 90% protein, 5% total fat, and 5% ash, according to the manufacturer.

Procedures

Acylation

Pulverized sawdust (5 g) was suspended in 1.0 M aq. NaOH solution (50 mL) at room temperature and

subsequently agitated for 24 h at room temperature in a closed flask. Subsequently, deionized water (125 mL) and 0.1 mole of one of the following acyl anhydrides were admixed to each suspension at room temperature: glutaric, maleic, phthallic, and succinic anhydride. The reaction mixture was subsequently agitated for 24 hours in a sealed flask at room temperature, followed by room temperature centrifugation (30 min at 6000 rpm). Supernatants were decanted and the resulting centrifuge cakes were dried in air at 50°C.

Carboxymethylation

Pulverized sawdust (5 g) was suspended in deionized water (175 mL) at room temperature, and solid NaOH (4.5 g) was subsequently added. The reaction mixture was agitated for 24 h at room temperature in a closed flask, followed by the addition of sodium chloroacetate (0.1 mole). The reaction mixture was subsequently agitated for 24 h in a sealed flask at room temperature, followed by room temperature centrifugation (30 min at 6000 rpm). Supernatants were decanted and the resulting centrifuge cakes were dried in air at 50°C.

Control Samples

The following control formulations were prepared: (1) pulverized sawdust powder (5 g) suspended in deionized water (50 mL) and agitated for 24 h at room temperature; (2) pulverized sawdust powder (5 g) suspended in 1.0 M aq. NaOH solution (50 mL) and agitated for 24 h at room temperature; (3) formulation (2) above subsequently derivatized by each of the acylation and carboxymethylation procedures described above; (4) soy protein isolate (5 g) dissolved in deionized water (100 mL) and agitated for 24 h; (5) sample (1) above subsequently mixed with sample (4) above for 24 h at room temperature; and (6) sample (2) above subsequently mixed with sample (4) above for 24 h at room temperature. Mixtures (1) to (6) above subsequently underwent room temperature centrifugation (30 min at 6000 rpm). Supernatants were subsequently decanted and the resulting centrifuge cakes were transferred with a spatula into a pellet mold placed on a flat ceramic surface at room temperature. The mold consisted of a flat acrylic sheet (8 mm thickness) perforated with individual holes (12.5 mm diameter). The filled mold was subsequently dried in air at room temperature for 24 h.

Reactions of Derivatized Hardwood and Soy Protein Isolate

Soy protein isolate (5 g) was dissolved in deionized water (100 mL), and derivatized sawdust (5 g) was admixed at room temperature. The reaction mixture was agitated for 24 h in a sealed flask at room temperature, followed by room temperature centrifugation (30 min at 6000 rpm). Supernatants were decanted and the resulting centrifuge cakes were transferred with a spatula into the same pellet mold described above. The filled mold was subsequently dried in air at room temperature for 24 h. Moist pellets were then transferred to an oven and dried in air at 50°C. Ten pellets were prepared from each compound for subsequent mechanical property measurements.

IR Spectra

Infrared spectra were measured using a Bruker Equinox 55 (Bruker, Madison, Wisconsin, U.S.A.) FTIR spectrometer fitted with a Pike Technologies ATR attachment. Spectra were recorded with 32 scans at 4 cm^{-1} resolution at room temperature.

Differential Scanning Calorimetry

Samples were evaluated with a DSC 550E (Instrument Specialists Inc. Spring Grove, Illinois, USA) from room temperature to 250°C at a heating rate of 20°C/min. These measurements were obtained on solid samples contained in open pans in a stream of nitrogen.

Mechanical Properties Tests

Tensile strengths of individual pellets were measured by the diametric compression method [60]. Individual pellets were compressed between flat compression platens in a computer-instrumented mechanical testing machine (model 1125, Instron Corp., Canton, Massachusetts, USA). At least 10 separate specimens of each specimen composition were subjected to mechanical testing at room temperature. During each test, the displacement rate of the compression platens was 5 mm/min. Load versus displacement data were computer recorded for each compression test. The fracture strength, σ_f, of each specimen was determined by the following formula [60]:

$$\sigma_f = 2P/(\pi D t) \tag{1}$$

In this expression, P is the load at fracture, D is the pellet diameter, and t is the pellet thickness.

RESULTS AND DISCUSSION

The derivatization of sawdust and the subsequent formation of reaction products with soy protein isolate were monitored by IR spectroscopy. The observed changes were similar to our observations of reactions with corn distillers'dry grain [1] and corncob powder [2]. As shown in the top spectrum in Fig. 1, the as-received and pulverized sawdust exhibited a relatively strong group of bands from 1000 up to 1700 cm^{-1} corresponding to C—O stretching, hydroxyl bending, and carbonyl stretching [61].

The reaction of sawdust with glutaric anhydride and subsequently with soy protein isolate produced the IR spectrum which is presented in the middle of Fig. 1. For comparison purposes, the spectrum of the same, as-received soy protein isolate can be observed in the first paper in this series [1]. Evident in Fig. 1 is the appearance of C=O peaks from the glutaryl moiety as well as typical protein bands. Also evident are C—H and O—H stretching bands near 2900 and 3400 cm^{-1}. These results support the hypothesis of the formation of glutarated sawdust complexes with soy protein. Essentially the same IR spectroscopy

results were observed for all other acylated sawdust complexes with soy protein isolate (not shown).

Carboxymethylation of sawdust followed by reaction with soy protein isolate produced changes in the spectrum between 1400 and 1700 cm^{-1} (bottom spectrum in Fig. 1). These spectral occurrences suggested the possible formation of a complex of carboxymethylated sawdust and soy protein isolate.

Differential scanning calorimetry provided data of low precision, because corresponding endothermic peaks were broad and shallow. As-received and pulverized sawdust that was not previously soaked in NaOH exhibited onset and peak temperatures at approximately 129.1 and 143.5°C, respectively, with a corresponding enthalpy change of 2.45 J/g. Derivatization of sawdust and subsequent reaction with soy protein isolate produced materials of lower onset and peak temperatures, however, the enthalpy changes increased by an order of magnitude for all methods of derivatization. In turn, this suggests the possible formation of complexes of protein and derivatized sawdust.

Blending of soy protein isolate with each of the derivatized sawdust specimens resulted in instant precipitation of gels. This suggests the possibility of protein complexing with anionized polysaccharides in sawdust. Centrifugation of all specimens yielded
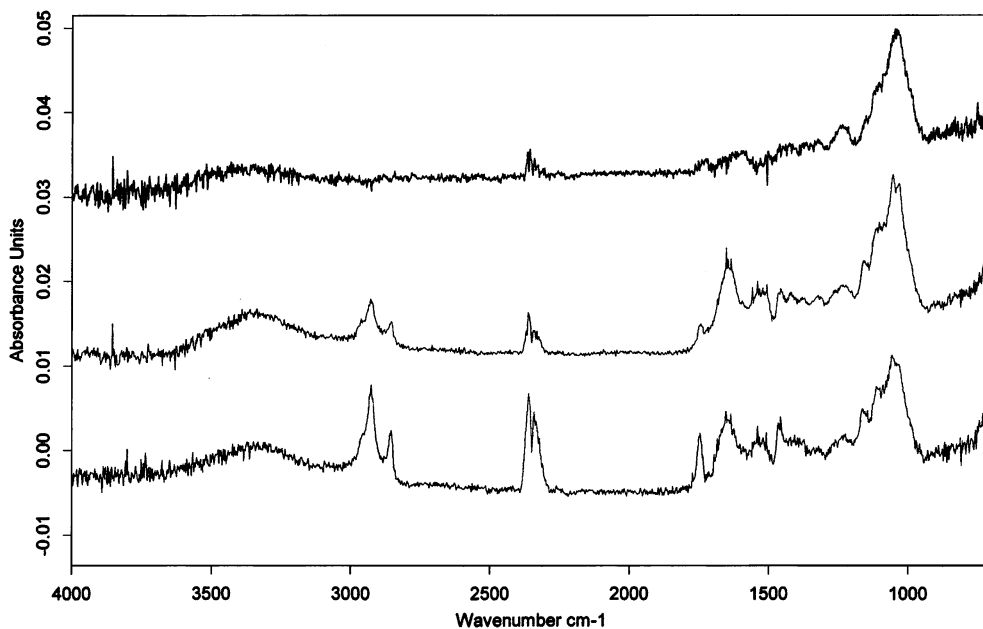

Fig. 1. Infrared spectrum of hardwood powder (top), the reaction product of glutarated sawdust with soy protein isolate (middle), and the reaction product of carboxymethylated sawdust with soy protein isolate (bottom). The peak near 2350 cm^{-1} is due to the asymmetrical stretching vibration of CO_2, which is present as a result of the ATR attachment being exposed to the laboratory atmosphere.

supernatants that were transparent to the naked eye. In all cases, centrifuge cakes had a viscous, paste-like consistency and were easily smeared into pellet molds with a hand-held laboratory spatula.

Hard solids were made from drying all pastes that were previously isolated from aqueous suspensions of protein mixed with derivatized sawdust, regardless of the method of derivatization. This also suggests the possibility of protein complexing with anionized polysaccharides in sawdust.

Pellets dried from control formulations (1) to (5) disintegrated into loose powder. In contrast, control sample (6) (nonderivatized sawdust, soaked in NaOH and protein) dried into a solid having a relatively low tensile strength of 0.9 MPa (Table I). Previously, we prepared control samples made of soy protein isolate blended with either non-derivatized distiller's dry grain [1] or non-derivatized corncob powder [2]. In both of those cases, dried pellets disintegrated into loose powder, thereby suggesting the absence of complexation between soy protein isolate and non-derivatized polysaccharides in those samples. We do not fully understand the exact reason why a hard solid formed upon blending protein with non-derivatized sawdust in control sample (6) above. We speculate that protein may have complexed with the lignin present in sawdust, given that this lignin is disposed with some anionic properties.

Table I illustrates the effects of the type of derivatization on the drying shrinkages and the mechanical properties of the reaction products between derivatized sawdust and soy protein isolate. We did not observe significant trends in sample composition on drying shrinkage. Glutaration and maleiation resulted in pellets with the highest strengths of up to 2.4 MPa. As shown in Table I, each composition exhibited significant variability in tensile strength. Also shown in Table I, we did not observe significant increases in tensile strengths compared to those of control sample (6).

Tensile strengths in Table I are relatively low as compared with traditional, petroleum-derived engineering plastics. For example, polytetrafluorethylene and high-density polyethylene have strengths that range between 20 to 35 MPa; butadiene-acrylonitrile and butadiene-styrene elastomers have strengths that range between 7 to 20 MPa [62]. By comparison, biodegradable soy protein plastics have been reported with strengths between 23.6 and 42 MPa [26].

Upon drying, all pellets exhibited microscopic pores of approximately 300–700 microns in size, based on optical microscopy observations. It is proven from fracture mechanics theory that microstructural pores function as stress concentrators that reduce the tensile strength of a broad range of engineering materials, including metals and plastics [63–64]. Fracture mechanics theory also proves that reducing the pore size can significantly increase tensile strength. It is possible that high pressure filtration, instead of centrifugation, could consolidate gels into higher density pastes prior to drying. In turn, the formation of smaller pores during subsequent drying would be likely, thereby increasing tensile strength. There is precedent for this behavior in industrial processes involving the dewatering and subsequent drying of liquid suspensions of inorganic colloidal solids [65–67]. Additional research is needed to validate this hypothesis for the sawdust-protein reaction products in this study.

CONCLUSIONS

Hardwood sawdust was derivatized by carboxymethylation with chloroacetic acid or by acylation with either glutaric, maleic, phthallic, and succinic anhydride. Blending of all derivatized sawdust

Table I. Drying Shrinkages and Tensile Strengths of Reaction Products of Soy Protein Isolate with Derivatized Sawdust

Method of derivatization	Pellet dimensions after drying shrinkage[a,b]		Mean Tensile Strength[b] (MPa)
	Diameter (mm)	Thickness (mm)	
Control sample (6)[c]	11.1 ± 0.5	7.5 ± 0.6	0.9 ± 0.5
Carboxymethylated	10.9 ± 0.8	5.7 ± 0.9	1.6 ± 1.2
Glutarated	10.7 ± 0.7	6.9 ± 0.6	1.3 ± 1.0
Maleiated	10.1 ± 0.4	6.2 ± 0.6	2.4 ± 0.8
Phthallated	10.7 ± 0.4	6.6 ± 0.7	1.3 ± 0.7
Succinylated	10.8 ± 0.4	6.7 ± 0.3	1.4 ± 0.5

[a]Original dimensions of pellets were 12.5 mm diameter × 8 mm thick.
[b]Standard deviation appears to the right of the ± symbol.
[c]Non-derivatized sawdust soaked in NaOH followed by blending with soy protein.

specimens with soy protein isolate resulted in instant precipitation of gels. Infrared spectroscopy and differential scanning calorimetry suggested the formation of complexes between soy protein isolate and each of the derivatized sawdust specimens. Specimens of protein reacted with anionic sawdust exhibited tensile strengths of up to 2.4 MPa, suggesting that these materials could be promising candidates for biodegradable structural materials.

ACKNOWLEDGMENTS

REFERENCES

1. C.H. Schilling, P. Tomasik, D. S. Karpovich, B. Hart, S. Shepardson, J. Garcha, and P. T. Boettcher (2004) *J. Polym. Environ.* **12**, 257–264.
2. C. H. Schilling, P. Tomasik, D. S. Karpovich, B. Hart, J. Garcha, and P. T. Boettcher (2005) *J. Polym. Environ.* **13**, 57–63.
3. C. H. Schilling, P. Tomasik, D. S. Karpovich, B. Hart, J. Garcha, and P. T. Boettcher, *J. Polym. Environ.*, in press.
4. E. S. Stevens (2002) *Green Plastics: An Introduction to the New Science of Biodegradable Plastics,* Princeton University Press, Princeton, NJ.
5. G. Scott (1995) *Degradable Polymers*, Chapman & Hall, New York, pp. 44–50.
6. R. A. Gross and B. Kalra (2002) *Science* **297**, 803–807.
7. Y. Poirier, D. E. Dennis, K. Klomparins, and C. Somerville (1992) *Science* **256**, 520–622.
8. C. Okkerse and H. van Bekkum (1996). *Starch 96* (H. van Doren and N. van Swaaj, Eds.), Zestec bv/Carbohydrate Research Foundation, Ch.1.
9. H. Ruck, (1996). *ywn. Technol. Jakoœœ,* **2**(7) Suppl, 138–157.
10. P. Tomasik, M. Pałasiñski, and S. Wiejak (1989) *Adv. Carbohydr. Chem. Biochem.* **47***,* 203–278.
11. 11.
    P. Tomasik, S. Wiejak, and M. Pałasinski (1989) *Adv. Carbohydr. Chem. Biochem.* **47**, 279–344.
12. P. Tomasik and C. H. Schilling (1998). *Adv. Carbohydr. Chem. Biochem.,* **53**, 263–343.
13. P. Tomasik and C. H. Schilling (1998). *Adv. Carbohydr. Chem. Biochem.* **53**, 345–426.
14. P. Tomasik and C. H. Schilling (2004). *Adv. Carbohydr. Chem. Biochem.* **59**, 175–403.
15. P. Tomasik and M. F. Zaranyika (1995) *Adv. Carbohydr. Chem. Biochem.* **51**, 243–318.
16. A. C. Albertson and B. Ranby (1979) *J .Appl. Polym. Sci.* **35**, 413–430.
17. J. G. Batelaan and P. M. Van der Horst (2000) U.S. Patent 6,103,885.
18. J. A. Youngquist, A. M. Krzysik, B. W. English, H. N. Spelter, and P. Chow (1996) *Proc. Symp. The Use of Recycled, Wood, and Paper in Building Applications, Madison,* WI. pp. 123–134.
19. R. M. Rowell, A. R. Sanadi, D. T. Caufield, and R. E. Jacobson (1997) *Lignocellulosic Plastic Composites* (A. L. Leao, F. X. Carvalho, and E. Frollini, Eds.), Uniiversidad de Sao Paulo, Sao Paulo, pp. 23–51.
20. P. J. Andersen and S. K. Hodson (2001) US Patent 6,231,970.
21. J. A. Youngquist, B. E. English, ZR. C. Schramer, Poo Chow, and R. S. Shooh (1998) *US Department of Agriculture, General Technical Report FPL-GTR-80.*
22. J. L.Wilett and W. M. Doane (2001) US Patent 6,362,256.
23. L. A. Johnson, D. J. Myers, and D. J. Burden (1992) *Inform* **3**(3), 282–290.
24. A. Satkofsky (2002) *J. Comp. Org. Recycl.* **43**(3), 60.
25. J. Jane and S. T. Tim (1995) *Progresss in Plant Polymeric Carbohydrate Research* (F. Meuser, D. J. Munnes, and W. Seibel, Eds.), Behr's Verlag, Hamburg, pp. 165–168.
26. C. H. Schilling, T. Babcock, S.Wang, and J. Jane (1995) *J. Mater. Res.* **10**, 2197–2202.
27. J. Zhang, P. Mungara, and J. Jane (2000) *Polymer* **42**, 2569–2578.
28. I. Pateau, C. A. Chen, and J. Jane (1994) *Ind. Eng. Chem. Res.* 33 1821–1827.
29. J. Jane and S. Zhang (1995) U.S. Patent 5,710,190.
30. J. Jane and K. Spence (1995) U.S. Patent 5,397,834.
31. S. K. Samant, R. S. Singhal, P. R. Kulkarni, and D. V. Rege (1993) *Int. J. Food Sci. Technol.* **28**, 547–562.
32. C. Schmitt, C. Sanchez, S. Desobry-Banon, and J. Hardy (1998) *Crit. Rev. Food Sci. Nutr.* **38**, 689–733.
33. H. Zaleska, P. Tomasik, S. G. Ring, (2001) *Carbohydr. Polym.* **45**, 89–94.
34. Zaleska H., Ring S. G., Tomasik P. (2001) *Int. J. Food Sci. Technol.,* **36**, 509–515.
35. T. Grega D. Najgebauer M. Sady P. Tomasik, and M. Faryna (2003) *J. Polym. Environ.* **11**, 75–83.
36. A. Dejewska, J. Mazurkiewicz, P. Tomasik, and H. Zaleska, (1995) *Starch/Staerke* **47**, 219–223.
37. H. Zaleska, J. Mazurkiewicz, P. Tomasik, M. Baczkowicz (1999) *Nahrung* **43**, 278–283.
38. H. Zaleska, S. G. Ring, and P. Tomasik, (2000) *Food Hydrocoll.* **14**, 371–382.
39. C.Y. Lii, H. H. Chan, and P. Tomasik (2003) *J. Polym. Environ.* **11**, 115–121.
40. C. Y. Lii, H. H. Chan, S. Lu, and P. Tomasik (2003) *Int. J. Food Sci. Technol.* **38**, 787–793.
41. C. Y. Lii, S. C. Liaw, and V. M.-F. Lai, P. Tomasik, (2002) *Eur. Polym. J.* **38**, 1377–1381.
42. C. Y. Lii, S. C. Liaw, and P. Tomasik, (2003) *Pol. J. Food Nutr. Sci.* **12/3**, 25–29.
43. C. Y. Lii, P. Tomasik, H. Zaleska, and S. C. Liaw, (2002) *Carbohydr. Polym.* **50**, 19–26.
44. H. Zaleska, P. Tomasik, and S. C. Lii (2002) *J. Food Eng.* **14**, 215–224.
45. H. Zaleska, P. Tomasik, and C. Y. Lii (2002) *Carbohydr. Polym.* **53**, 249–257.
46. T. Grega D. Najgebauer, M. Sady, and P. Tomasik (2003) *J. Polym. Environ.* **12**, 17–25.
47. T. Kitamura and H. Katayama (1999) *Proc. REWAS 99 Symp. San Sebastian Sept. 5–9 1999.* vol. 3, (I. Gabellah, J. Hager, and R. Solozabal, Eds.), Metals & Materials Soc, Warrendale, PA, pp. 2021–2028.
48. G. Lu, Q. Wang, K. Sakamoto, H. Kim, J. Naruse, J. Yuan, T, Maruyama, M. Kanude, and M. Sadakata (2000) *Energy, Fuel* **14**, 1133–1138.
49. T. Ohtsuka (1999) Jpn. Kokai Tokkyo Koho, 113 33420; *Chem. Abstr.* **132**, 24041.
50. W. S. Andrew, Jr. (1998) US Patent 5 728, 192.
51. H. Tanaka (2001) Jpn. Kokai Tokkyo Koho, 2002145686; *Chem. Abstr.* **136**, 406170.
52. J. Xu, T. Li, Y. Yan, and Z. Ren (1999) *Ranliao Huaxue Xuebao* 27, 328–334; *Chem.Abstr.* **131**, 301308.

53. G. Hartel, S. Roatz, and M. Schrey (1999) *Freib. Forschungshef*. **A852**, 243–257.
54. A. Nag (1995) *Proc. Saf. Environ. Protect*, **73** (B4), 299–304.
55. D. N. Thompson, R. L. Sayer, and K.S. Noah (2000) *Minerals, Metalurg. Proc*. **17**, 96–104.
56. N. Marcovich, M. M. Reboredo, and M. T. Aranguren (1997) *Proc. Int. Symp. Lignocellulosic Plastic Composites, Sao Paulo, Mar. 13–115, 1996* (A. L. Leao, F. X. Carvalho, and E. Frollini, Eds.), Universidade de Sao Paulo, Sao Paulo, pp. 223–240.
57. G. R. Rech, S. L. Vieira, G. A. Carvalho, M. Zeni, and J. A. Zattera (1998) *Proc. Int. l Symp. Natural Polymer and Composites, Atibaia, May 10–13, 1998,* (H. C. Mattosol, E. Frollini, and A. L. Leao, Eds), Embraya Agricultural Instrumentation, Sao Carlos, pp. 111–114.
58. A. S. Cherbakov, L. V. Golzeva, S. V. Podtyufarov, V. I. Kucherzoi, and V. S. Podtyufarov (1997) Jpn. Kokai Tokkyo Koho 09086999; *Chem. Abstr*. **127**, 180110.
59. Z. Kin (1971) *Lignin, Chemistry and Uses* (in Polish), WNT, Warsaw, Ch. 1 and 2.
60. D. Bortzmeyer (1992) *J. Mater. Sci*. **27**, 3305–3308.
61. R. M. Silverstein, G. C. Basler, and T. C. Morrill (1991) *Spectrometric Identification of Organic Compounds, 5th Edn*. John Wiley & Sons, New York.
62. W. D. Callister (2000) *Materials Science and Engineering, An Introduction, 5th Edn*. Wiley, New York, pp. 800–801.
63. R. W. Hertzberg (1996) *Deformation and Fracture Mechanics of Engineering Materials, 4th Edn* Wiley, New York, pp. 315–321.
64. L. J. Gibson and M. F. Ashby (1988) *Cellular Solids, Structure and Properties – 2nd Edn*. Cambridge University Press, Cambridge, UK, pp. 219–222.
65. J. S. Reed (1991). 'Drying,'' in *Engineered Materials Handbook, Volume 4, Ceramics and Glasses,* (S. J. Schneider Ed.), ASM International, Metals Park, Ohio, pp. 130–134.
66. G. Y. Onoda (1976) *J. Am. Ceram. Soc*. **58**, 236–39.
67. C. H. Schilling, V. J. Garcia, R. M. Smith, and R. A. Roberts (1998) *J. Am. Ceram. Soc*. **81**, 2629–269.