

Properties of Ozonized Soybean Oil/ Polymeric Methylenediphenyl-4, 4'-Diisocyanate Adhesives and Their Adhesion Performance for Wood

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Abstract

Ozonized soybean oil (OZSBO), obtained by the ozone cleavage reaction of the double bond of soybean oil, was reacted with polymeric methylenediphenyl-4,4'-diisocyanate (pMDI) to prepare wood adhesive. To investigate the feasibility of this preparation method, different polyurethane adhesives were prepared with a variety of equivalent molar ratios (eq-MRs) of OZSBO to pMDI. The chemical reactions of the adhesives were analyzed using Fourier transform infrared, and their thermal characteristics were investigated by differential scanning calorimetry and thermogravimetric analysis. The OZSBO/pMDI resins with eq-MRs of 1:0.5, 1:0.75, and 1:1 showed an exothermic reaction at 150°C, resins with eq-MRs of 1:2 and 1:3 exhibited exothermic peaks at 185°C, and resins with an eq-MR of 1:4 presented an exothermic peak at 180°C. The maximum adhesion strength was reached when plywood was bonded using the adhesive with an eq-MR of 1:2. This result shows that adhesion strength was not proportionally increased with the addition of pMDI after an eq-MR of 1:2, indicating that adhesion strength was attributed not only to reactions of the residual –NCO groups in the adhesive with the hydroxyl groups of wood during the manufacturing of plywood but also to the cross-linking reaction between OZSBO and pMDI.

Polyurethane (PU) adhesives show superior adhesion performance in wood materials, and their high functional performance facilitates their use for binding high-moisture-content woods and hence for structural applications of wood-based composites (Gamo 1984, Pizzi et al. 1993, Khan et al. 2004, Langmaier et al. 2005). Isocyanate-based PU resins have been especially regarded as non-formaldehyde-releasing resins (Aranguren et al. 2006, Soares et al. 2008). The wood industry is focused on using such resins because formaldehyde emission problems have been caused mostly by the release of formaldehyde. However, high cost, particularly the high price of polyol, is a limiting factor in the use of isocyanate-based PU resins. Therefore, the use of vegetable oil as a natural organic compound to replace polyol has been proposed (Aranguren et al. 2006). Mechanical properties and morphological structure of PU depend mainly not only on polyol structure and molar mass but also on the properties of isocyanates. Recently, some work on soybean oil (SBO)–PU adhesive for wood applications has been completed (Choi et al. 2011).

Other efforts have been made to improve adhesion by using modified polyols (Park et al. 2004, Pechar et al. 2006). Choi et al. (2011) obtained multihydroxy-epoxidized SBO via a ring-opening reaction with ethylene glycol by

introducing multihydroxy groups into vegetable oil, which provided a highly reactive precursor for reaction with polymeric methylenediphenyl-4,4'-diisocyanate (pMDI). Vegetable oils (Petrović et al. 2000, Somani et al. 2003) have been used to produce a PU resin for wood by refining the oils into glycerol and fatty acids and then reacting them with isocyanate to evaluate their bond strength with polybutylene. Formaldehyde-based resins, such as phenol-formaldehyde (PF) and urea-formaldehyde (UF), have been also shown to copolymerize with pMDI (Simon et al. 2002, Kang et al. 2007). Double bonds of vegetable oil can be oxidized with ozone to form aldehydes and/or carboxylic acids, depending on the work-up condition. In contrast to PF

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and UF resins, it is unclear whether those ozonized vegetable oils containing aldehydes and/or carboxylic acids as main components are also capable of reacting with pMDI and giving improved panel strength. We hypothesized that ozonized oils would be ideal for wood adhesives by reacting with isocyanate functional groups of pMDI-forming amides and imine bonds.

This study was conducted to evaluate the possibility of using ozonized SBO (OZSBO)/pMDI resin as a wood adhesive. OZSBO, which was obtained from SBO with ozonization, was reacted with pMDI resin at different equivalent molar ratios (eq-MRs) to prepare the adhesives. Here we present the results of an investigation that has led to the synthesis of a series of OZSBO/pMDI adhesives and their properties characterized by Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) to determine the optimum eq-MR. The bond performance of these adhesives in wood applications was measured using a standard method.

Experimental

Materials

SBO was purchased from CJ Co. The pMDI, with molecular weights ranging from 300 to 400, a viscosity of 192 mPa s^{-1} (at 23°C), a functionality of 2.7, and an equivalence of 133.3, was a gift from a local urethane foam board manufacturer (BASF Co.).

Ozonification of SBO

SBO (50 mL) was dissolved in acetone (450 mL) and stirred with a magnetic stirrer in an ozonizer (model Lab-2 [220 Vac, 60 Hz], Ozonotech Co., Daejeon, Korea), which had a flux of $0.5 \text{ liter min}^{-1}$ and a pressure of 1 kg cm^{-2} . Ozonification was conducted at an ozone density of 158.5 to 158.8 g cm^{-3} , ozone production of 7.13 to 7.14 g h^{-1} , and ozone time of 1, 2, and 3 h. After ozonification, it was concentrated at 70°C to eliminate acetone and then used as the raw material for the adhesives and analytical samples.

Plywood preparation

To determine the most effective mixing ratio in the production of the OZSBO/pMDI adhesive, each mixture was used to fabricate plywood, and the resulting bonding performance was evaluated. Lauan (Dipterocarpaceae, specific gravity 0.54) with a moisture content of 6 percent was used for the production of plywood with thicknesses of 1.2 mm for the face and 1.2 mm for the core. Each veneer, obtained by rotary cut, was cut into 350 by 350-mm pieces to construct a three-plywood composite with veneers of 1.2 mm for the face, 1.2 mm for the core, and 1.2 mm for the other face. Each adhesive mixture was applied on one side of the veneer with 150 g m^{-2} and thermally pressed at 67 s mm^{-1} with a pressure of 10 kgf at 150°C . The samples were prepared with eq-MRs of OZSBO to pMDI of 1:0.5, 1:0.75, 1:1, 1:2, 1:3, and 1:4. The final plywood's bond strength was measured with respect to Korean standard KS M 3720 (Korean Standards Association 2008).

Measurements

FTIR spectroscopy was used to confirm the presence of functional groups on the polymers. FTIR spectra were recorded as KBr pellets using a MIDAC FTIR spectrometer

at a resolution of 4 cm^{-1} with a spectral range of 400 to $4,000 \text{ cm}^{-1}$. DSC was conducted using a Perkin-Elmer DSC7, calibrated with indium, at a temperature range of 30°C to 350°C under a nitrogen atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$. The second-run DSC studies were performed with the following procedure: initial heating up to 250°C , quenching, and heating up to 300°C . TGA was performed in a Perkin-Elmer TGA7 at a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen gas flow rate of 50 mL min^{-1} , and both the maximum and the onset degradation temperatures were reported. The tensile strength of the plywoods was measured in a dry condition in a universal test machine (H 50K-Ss, Hounsfield, UK) at a strain rate of 2 mm min^{-1} . The tensile shear adhesive test was carried out according to KS M 3720, which is useful for face veneers with a thickness less than 1.6 mm. Samples of the dry test were measured 36 times for each eq-MR of OZSBO to pMDI of 1:0.5, 1:0.75, 1:1, 1:2, 1:3, and 1:4 without any further changes in the experimental conditions.

Results and Discussion

Synthesis of OZSBO

OZSBO provides a highly reactive precursor for reaction with pMDI. OZSBO was obtained by ozone cleavage reaction of the double bond of SBO, as shown in Figure 1. The reaction with pMDI (isocyanate) and OZSBO (carboxyl groups) leads directly to the formation of thermally and hydrolytically stable amide and C=N bonds so that the formed amide adhesives provide a flexible structure with the help of aliphatic long chains and typically proceed to high conversions without the formation of by-products. The proposed reaction mechanism is shown in Figure 2.

Figure 3 shows the FTIR spectra and presents the characteristic peaks for the ozonification time of SBO. The absorption bands of 1 h OZSBO appeared within $1,720$ to $1,700 \text{ cm}^{-1}$ for C=O, at $1,500 \text{ cm}^{-1}$ for C=C, within $3,000$ to $2,800 \text{ cm}^{-1}$ for -CH (sp^3 mixture), within $3,010$ to $3,000 \text{ cm}^{-1}$ for =C-H (sp^2 mixture), and within $3,500$ to $3,300 \text{ cm}^{-1}$ for -OH bonds. In 2 h OZSBO, the =C-H (sp^2) band appeared as a shoulder of the -OH band due to the small absorption bands for =C-H within $3,010$ to $3,000 \text{ cm}^{-1}$ covered by the huge -OH band. In 3 h OZSBO, the hydroxyl absorption band increased broadly within $3,500$ to $3,300 \text{ cm}^{-1}$, while the ethylene band within $1,620$ to $1,600 \text{ cm}^{-1}$ disappeared due to the ozonolysis.

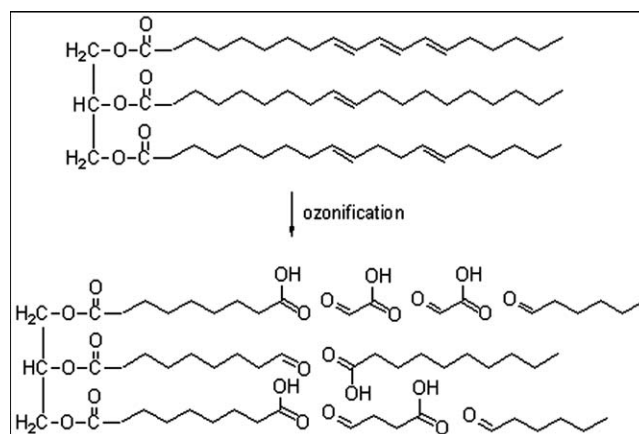


Figure 1.—Synthesis of ozonized soybean oil (OZSBO).

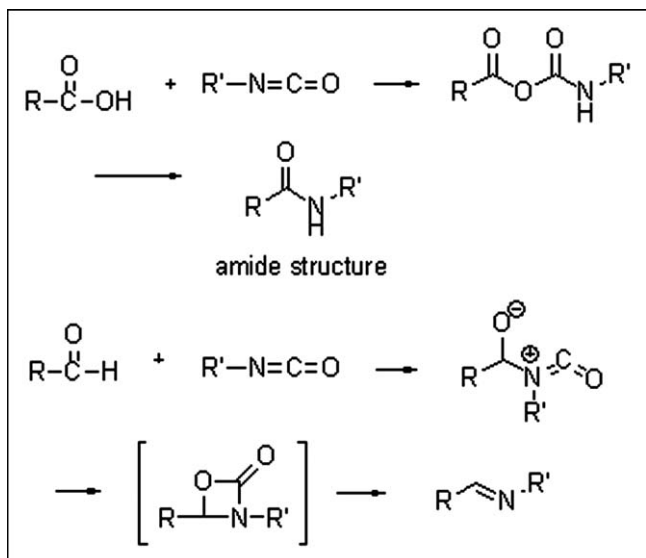


Figure 2.—Proposed reaction mechanism of ozonized soybean oil (OZSBO) and polymeric methylene-diphenyl-4,4'-diisocyanate (pMDI).

FTIR spectra of OZSBO/pMDI prepolymer resins

To examine the chemical reaction between OZSBO and pMDI, OZSBO and pMDI were mixed at different eq-MRs (1:0.5, 1:0.75, 1:1, 1:2, 1:3, and 1:4) and then subjected to FTIR scans. The MRs were calculated based on the eq-MR of the hydroxyl and isocyanate groups in OZSBO/pMDI.

Figure 4 shows different intensities of the absorption bands of the hydroxyl and $-NCO$ groups, which are generally presented at $3,400$ and $2,300\text{ cm}^{-1}$, respectively. With increasing pMDI content, the peak intensity of the hydroxyl groups decreased and that of the $-NCO$ groups increased. The ester carbonyl peak of the OZSBO/pMDI resins occurred at $1,760\text{ cm}^{-1}$. The absorption bands at $1,500\text{ cm}^{-1}$ were assigned to the mixture of $C=N$ and the carbonyl stretching of urethane and amide. The bonds

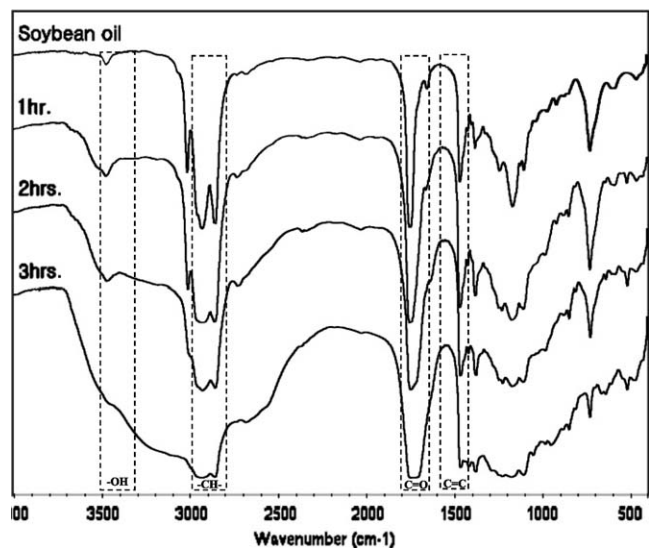


Figure 3.—Fourier transform infrared (FTIR) spectra of soybean oil and ozonized soybean oil (OZSBO).

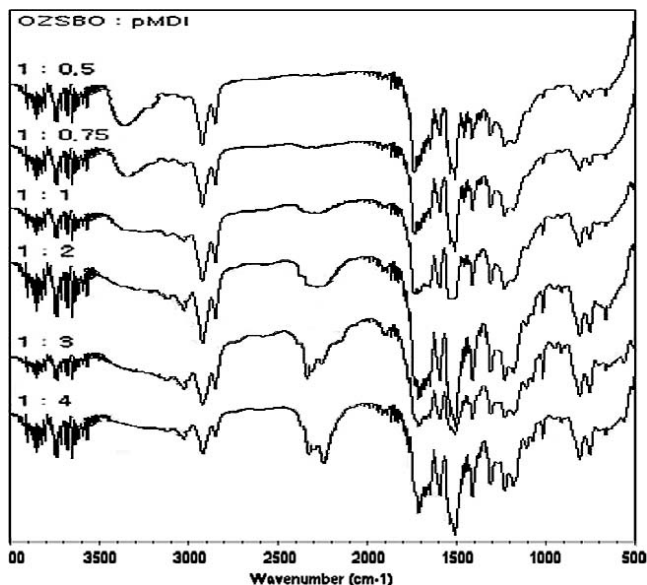


Figure 4.—Fourier transform infrared (FTIR) spectra of ozonized soybean oil (OZSBO)/polymeric methylene-diphenyl-4,4'-diisocyanate (pMDI) resins as a function of mixing ratio.

within 750 to $1,150\text{ cm}^{-1}$ were attributed to the C-H absorption bands of $-CH_2$ and $-CH_3$, C-O, and C-N. The adequate amount of hydroxyl groups acted to control the reactivity and properties of the OZSBO/pMDI resins, depending on the various eq-MRs.

Thermal behaviors of OZSBO/pMDI resins

The thermo-oxidative stability of the OZSBO/pMDI resins was studied using TGA, and the results are shown in Figure 5. Most of the polymers showed good thermal stability at high temperature under a nitrogen atmosphere. The initial weight loss over 120°C was attributed to the formation of CO_2 as a by-product and at 300°C to that of functional groups, such as NCO and hydroxyl, that were released from the cross-linked polymer. The second weight loss over 300°C was assigned to the breakaway of urethane groups, which are linkages of polymer chains. The third weight loss over 480°C was assigned to the degradation of the polymer main chain. The weight loss at 300°C was

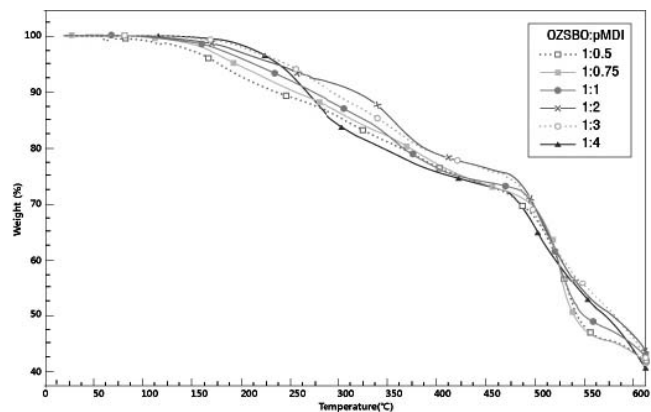


Figure 5.—Thermogravimetric analysis (TGA) curves of ozonized soybean oil (OZSBO)/polymeric methylene-diphenyl-4,4'-diisocyanate (pMDI) resins.

greatest at an eq-MR of 1:4 and least at 1:2, followed by 1:3. The increased weight loss by the higher eq-MR is caused by the larger amount of isocyanates, resulting in more unstable groups that can break down by heat.

The thermal behavior of the OZSBO/pMDI resins was investigated by preparing the samples at room temperature and conducting DSC at an ambient temperature of 25°C to 300°C. Figure 6 shows the DSC thermograms of the OZSBO/pMDI resins with different eq-MRs to compare their curing behaviors. The OZSBO/pMDI resins with eq-MRs of 1:0.5, 1:0.75, and 1:1 exhibited an exothermic reaction at 150°C, resins with eq-MRs of 1:2 and 1:3 showed exothermic peaks at 185°C and resins with an eq-MR of 1:4 presented an exothermic peak at 180°C.

The second-run DSC studies are presented in Figure 7. The strength of the OZSBO/pMDI resins due to their cross-linked polymers resulted in the absence of any observed thermal behaviors.

Adhesive bond strength

As shown in Figure 8, the bond strength almost reached a plateau at an eq-MR of 1:2, a result of the reaction between isocyanate and all the -OH groups in the wood and OZSBO. Sonnenschein and Wendt (2005) reported that the generation of polyurea compounds by the reaction of the -NCO group with the -OH group improves bond strength. In addition, Simon et al. (2002) reported a trend of increasing bond strength with increasing pMDI content. In our research, however, high isocyanate content (ratios of 1:3 and 1:4) did not increase bond strength, so an excess amount of isocyanate was not necessary. The bond strength attained in the present study was greater than that required in the Korea standard (7 kgf cm⁻² for broad-leafed trees and 6 kgf cm⁻² for needle-leafed trees) at an eq-MR of 1:2. These results were attributed to a greater number of -NCO groups in the OZSBO/pMDI resins, which created more bonds between the unreacted -NCO groups and the hydroxyl groups of cellulose in the plywood, changing them into urea bonds, biuret bonds, or urethane bonds under the heat of hot-pressing and thereby enhancing the resins' bending properties (Wendler and Frazier 1996, Wieland et al. 2006). The OZSBO/pMDI resins were demonstrated to be excellent candidates for adhesive applications.

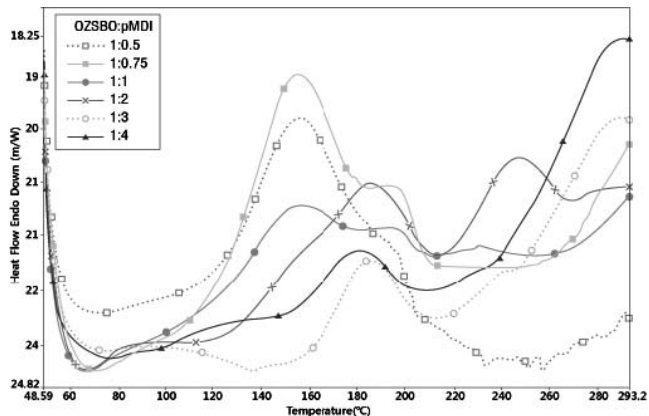


Figure 6.—Differential scanning calorimetry (DSC) curves of ozonized soybean oil (OZSBO)/polymeric methylene-diphenyl-4,4'-diisocyanate (pMDI) resins.

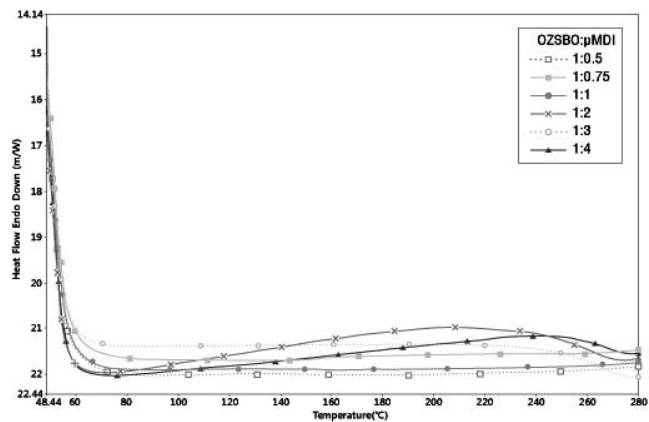


Figure 7.—Two-run differential scanning calorimetry (DSC) curves of ozonized soybean oil (OZSBO)/polymeric methylene-diphenyl-4,4'-diisocyanate (pMDI) resins.

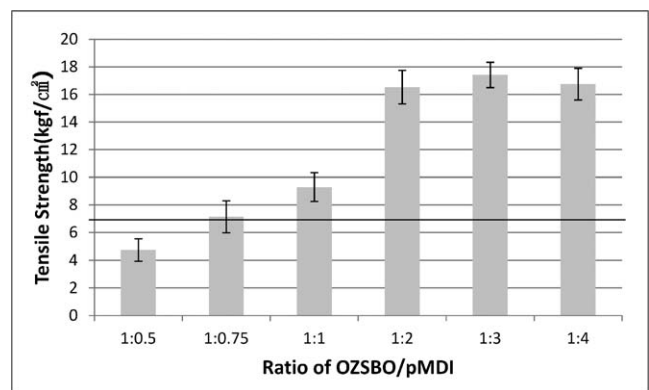


Figure 8.—Tensile strengths of ozonized soybean oil (OZSBO)/polymeric methylene-diphenyl-4,4'-diisocyanate (pMDI) resins.

Conclusions

The feasibility of developing wood adhesive by using OZSBO, ozonized from SBO, and pMDI was investigated. Adhesive resins with different eq-MRs of OZSBO and pMDI were chosen to determine an optimum condition for maximizing bonding strength. The chemical structure of the resins was analyzed with FTIR spectroscopy, and their thermal curing behavior was investigated using DSC and TGA. The OZSBO/pMDI resins with eq-MRs of 1:0.5, 1:0.75, and 1:1 exhibited exothermic reactions at 150°C, eq-MRs of 1:2 and 1:3 showed exothermic peaks at 185°C, and an eq-MR of 1:4 presented an exothermic peak at 180°C. This result shows that adhesion strength was not proportionally increased with the addition of pMDI; rather, maximum adhesion strength reached an eq-MR of about 1:2, indicating that at least two eq-MRs of pMDI over OZSBO are necessary to complete the cross-linking reactions among OZSBO, pMDI, and wood carbohydrates.

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Literature Cited

Aranguren, M. L., M. Mosiewiwicki, and J. B. Fernandez. 2006. Natural composites: Polymeric matrices based on vegetable resources. *Mol. Cryst. Liq. Cryst.* 448:747–761.

- Choi, S. W., D. W. Seo, Y. D. Lim, Y. G. Jeong, M. S. Islam Mollah, H. Park, T. W. Hong, and W. G. Kim. 2011. Synthesis and properties of multihydroxy soybean oil from soybean oil and polymeric methylene-diphenyl-4,4'-diisocyanate/multihydroxy soybean oil polyurethane adhesive to wood. *J. Appl. Polym. Sci.* 121:764–769.
- Gamo, M. 1984. Wood adhesives from natural raw materials. *J. Appl. Polym. Sci.* 40:101–126.
- Kang, E. C., S. B. Park, X. S. Sun, B. D. Park, and H. Park. 2007. Curing behavior of urea-formaldehyde resin modified with cooking waste oil-based pMDI prepolymer and its influence on particleboard properties. *Forest Prod. J.* 57(6):51–58.
- Khan, M. A., S. M. Ashraf, and V. P. Malhotra. 2004. Eucalyptus bark lignin substituted phenol formaldehyde adhesives: A study on optimization of reaction parameters and characterization. *J. Appl. Polym. Sci.* 92:3514–3523.
- Korean Standards Association (KSA). 2008. Testing methods for the strength properties of adhesives for wood in shear by tension loading for ordinary plywood. KSA, Seoul, South Korea.
- Langmaier, F., K. Kolomazník, M. Mládek, and J. Šivarová. 2005. Curing urea-formaldehyde adhesives with hydrolysates of chrome-tanned leather waste from leather production. *Int. J. Adhes. Adhes.* 25:101–108.
- Park, S. J., F. L. Jin, and J. R. Lee. 2004. Synthesis and thermal properties of epoxidized vegetable oil. *Macromol. Rapid Commun.* 25:724–727.
- Pechar, T. W., S. Sohn, G. L. Wilkes, S. Ghosh, C. E. Frazier, A. Fornof, and T. E. J. Long. 2006. Characterization and comparison of polyurethane networks prepared using soybean-based polyols with varying hydroxyl content and their blends with petroleum-based polyols. *J. Appl. Polym. Sci.* 101:1432–1443.
- Petrović, Z. S., A. Guo, and W. J. Zhang. 2000. Structure and properties of polyurethanes based on halogenated and nonhalogenated soy-polyols. *J. Polym. Sci. Part A Polym. Chem.* 38:4062–4069.
- Pizzi, A., J. Valenzuela, and C. Westermeyer. 1993. Non-emulsifiable, water-based, mixed diisocyanate adhesive systems for exterior plywood. Part II. Theory application and industrial results. *Holzfor-schung* 47:68–71.
- Simon, C., B. George, and A. Pizzi. 2002. Copolymerization in UF/pMDI adhesives networks. *J. Appl. Polym. Sci.* 86:3681–3688.
- Soares, B. G., V. Gonzalez, R. Galimberti, A. S. Sirqueira, F. L. Barcia, and R. A. Simvão. 2008. Toughening of an epoxy resin with an isocyanate-terminated polyether. *J. Appl. Polym. Sci.* 108:159–166.
- Somani, K. P., S. S. Kansara, N. K. Patel, and A. K. Rakshit. 2003. Castor oil based polyurethane adhesives for wood-to-wood bonding. *Int. J. Adhes. Adhes.* 23:269–275.
- Sonnenschein, M. F. and B. L. Wendt. 2005. Efficacy of polymeric MDI/Polyol mixtures for binding wood boards. *Wood Sci. Technol.* 39:27–36.
- Wendler, S. L. and C. E. Frazier. 1996. The effects of cure temperature and time on the isocyanate-wood adhesive bondline by ¹⁵N CP/MAS NMR. *Int. J. Adhes. Adhes.* 16:179–186.
- Wieland, S., A. Pizzi, S. Hill, W. Grigsby, and F. Pichelin. 2006. The reaction in water of UF resins with isocyanates at short curing times: A ¹³C NMR investigation. *J. Appl. Polym. Sci.* 100:1624–1632.