Investigating the Possibility of Making Lignin-glyoxal Resins as Adhesives in the Production of Plywood

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The possibility of making glues of natural origin (pure lignin and lignin-gluoxal) instead of chemical resins for making plywood from poplar layer was investigated. For this purpose, lignin was reacted with glyoxal and the lignin-glyoxal glue was produced. To make the desired plywood, pure lignin (L.100%), lignin-glyoxal 15% (L.85%, G.15%), and lignin-glyoxal 30% (L.70%, G.30%) were used as the adhesive at three different levels. Ammonium chloride (1%) as the hardener and wheat flour (30%) as the filler based on the dry weight of the adhesive were also used. Plates made with urea formaldehyde resin at 160 g/m^2 were considered as control samples. After the laboratory boards were produced, the physical and mechanical properties of samples, such as thickness swelling after 2 and 24 h of immersion in water, shear strength, modulus of rupture and modulus of elasticity, were measured. In addition, the groups and bonds in the pure lignin and lignin-gloxal adhesives were identified by Fourier transform infrared (FTIR) spectroscopy. In most tests and compared to the boards made of the adhesives and control boards, the lignin-glyoxal 30% (L.70%, G.30%) glue came closest to the performance of the control glue.

Keywords: Plywood; Adhesive; Lignin; Glyoxal; Ammonium chloride

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INTRODUCTION

The adhesive most often used in plywood is urea-formaldehyde, making it one of the most important and practical adhesives. Although this adhesive has some advantages, such as cheap cost, easy transfer and application, and good adhesiveness, it has some problems regarding formaldehyde emissions (during the pressing time and in application) and it also does not have proper strength against some atmospheric factors. Despite severe environmental controls, long-term exposure to formaldehyde can cause cancer and respiratory disease because of its toxicity (Enayati *et al.* 2009). To this end, many efforts have been made to reduce or eliminate formaldehyde release from wood products made with urea formaldehyde adhesives, including changes in the manufacturing of adhesives, changes in the type of catalyst used, and the use of additives during the manufacturing of the adhesive (El Mansouri *et al*. 2007b). The main stimulus for today's renewed interest in bio-based adhesives is the acute sensitivity of the general public toward anything concerning the environment and its protection (Pizzi 2006). However, use of synthetic resins limits somewhat the environmental attractivness of such adhesives based on purely natural materials, while the use of some natural materials such as tannins alone is currently limited by the relatively low supply of these materials (Pizzi 2006). Different waste lignins produced in pulp mills appear promising for conversion to phenolic precursors for phenol-based resins (Navarrete *et al.* 2012), and for the preparation of natural adhesives (El Mansouri *et al*. 2007b).

Several studies have been conducted in recent years on the use of spent pulp cooking liquor or the use of the resulting lignin as an adhesive, but nothing has been reported on the full use of the resulting lignin from soda pulping processes or modified liquor as an adhesive in the manufacturing of wooden products. The results of previous studies have shown that bagasse lignin has the capacity to substitute for up to 40% of the weight of phenol formaldehyde adhesive, and the mechanical strength of lignin-phenol formaldehyde adhesive panels is more than that of panels where only phenol formaldehyde adhesive has been used (Khan *et al.* 2004). Navarrete *et al.* (2012) reported that particleboards adhered with mixtures of kraft and wheat straw glyoxalated lignin with mimosa tannin and hexamine as a hardener. These particleboards were classified as interior panel P2 in according with the standard EN 312 1995 based on their highest IB strength. Glyoxalated lignin has been incorporated into PF resin, tannin, and polymethylene polyphenyl isocyanate (pMDI) to use as an adhesive in wood composites (El Mansouri *et al*. 2007b; Navarrete *et al.* 2012). El Mansuori *et al*. (2007b) produced an adhesive without formaldehyde propagation, and the internal adhesion of the board was higher than international standard specifications for exterior-grade panels. Several studies have been conducted on the effect of glyoxalization on various lignin properties, but no report has been made on the effect of this aldehyde on the structural changes in the lignin resulting from bagasse soda pulping. Therefore, the purpose of this study is to use pure lignin and lignin-glyoxal adhesives to replace the aldehyde-based urea adhesive in the production of plywood.

EXPERIMENTAL

Materials

In this research, 2-mm-thick poplar boards were provided from Amol Rookesh Factory (Amol, Iran). First, the boards were cut into 30 cm × 30 cm pieces and they were dried at 70 °C up to 3% relative humidity. Black liquor was obtained from the soda cooking of bagasse pulp at the Pars Papermaking Company (Haft-Tappeh, Khuzestan), and the required lignin was extracted *via* the acidification of black liquor (pH = 2) with sulfuric acid and based on the procedure by Lin and Dence (1992). The extracted lignin was thoroughly washed with distilled water and collected after being completely ground by the mill, and glyoxal with a concentration of 40% was purchased from Merck Company (Darmstadt, Germany). To make the lignin-glyoxal adhesive based on the method of El Mansuori *et al*. (2007a), lignin powder was first mixed with water until it was completely wet, then 30% sodium hydroxide solution was progressively added until the pH reached approximately 11. The mixture was then poured into a flask containing a condenser, thermometer, and magnetic mixer. Then 40% glyoxal was slowly and periodically added. The resulting solution was stirred at 60 °C for 8 h. At the end, the prepared adhesive was cooled to room temperature, collected, and its properties including pH, viscosity, solids materials, and density of the resulting adhesive were measured. The urea formaldehyde adhesive was prepared from Pars Neopan Nashtarood Company (Chalous, Iran), and its features are shown in Table 1.

Table 1. Features of Urea-formaldehyde and Lignin-glyoxal Adhesives

Resin Types	Solid Content (%)	Gel time (s)	Viscosity (°centipoises)	Density (g/cm^3)	pH
Urea-formaldehyde	60	146	1.25	1.26	7.6
Lignin-glyoxal	58	62	1.88	1.06	11

Methods

For the production of plywood, the surface layers (first and third) were placed together in the same direction without adhesive and the middle layer in the opposite perpendicular position (surface layer), accompanied with an adhesive. The adhesive used included pure lignin 100% (Lignin derived from black liquor bagasse soda), 15% lignin-glyoxal (85% pure lignin plus 15% glyoxal), and 30% lignin-glyoxal (70% pure lignin plus30% glyoxal) prepared according to the method of El Mansuori *et al*. (2007a). In fact, all three lignin adhesives were coated seperately in three levels: first as much as 120 g/m^2, then as much as 140 g/m^2, and finally as much as160 g/m^2 (the quantity of the adhesive used in manufacturing board in each levell) by screwdriver equally all over the board. Then, it was set at 160 °C with 50 bar pressure and 5 min press time. To balance the moisture content of the boards with the environment, they were kept in a conditioning room with a relative humidity of 65% and 20 °C temperature. In addition, ammonium chloride was used as the hardener at 1% concentration and wheat flour was used as the filler (30%). The boards produced using the urea-formaldehyde adhesive were considered the control samples at the 160 g/m^2 level. Then, the shear strength, modulus of elasticity, modulus of rupture, and thickness swelling were measured after 2 and 24 h based on BS EN 314-1 (2004), EN 310 (1993), and ISIRI 3492 (2003) standards using a Santam universal testing machine (Santam Company, Tehran, Iran).

Fourier-transform Infrared Spectroscopy (FT-IR)

FT-IR model of Shimadzu FTIR 8400S was used in Islamic Azad University, Department of Science and Research, Tehran in order to study the bonds and functional groups existed in pure lignin and modified with glyoxal. The absorption bands were assigned as suggested by Tejado *et al*. (2007), Laot (1997), and Schultz and Glasser (1986).

Statistical analysis

The statistical analysis was conducted using an SPSS programming method in conjunction with an analysis of variance (ANOVA); Duncan's multiple range test (DMRT) was used to test the statistical significance at an $\alpha = 0.05$ level using SPSS software (IBM Corporation, ver 21, Armonk, NY, USA).

RESULTS AND DISCUSSION

FTIR Analysis

The molecular structure changes of lignin were analyzed by FTIR Spectroscopy. The FTIR spectra of the original lignin produced as shown in Fig. 1, some characteristic absorption peaks can be seen clearly (1015 cm^{-1}, 1019 cm^{-1} and 2870 cm^{-1}). The spectra of both lignin samples show a relatively similar and common pattern. The structure of the studied lignins shows that after the glyoxalation of the lignin, the major peaks increased slightly. As shown in Fig. 1, three changes under the effect of lignin-glyoxalated were in the regions of 1015 cm^{-1}, 1119 cm^{-1}, and 2870 cm^{-1}. The peak region of 1015 cm^{-1} is related to the C-O tensile vibrations of aryl alkyl ethers. The peak region of 1119 cm^{-1} is related to the stretching vibrations of the C-O give data on methylene groups and ether bonds. And the peak region of 2870 cm^{-1} is related to the C-H stretching vibration of the methylene in the lignin-glyoxal adhesive.

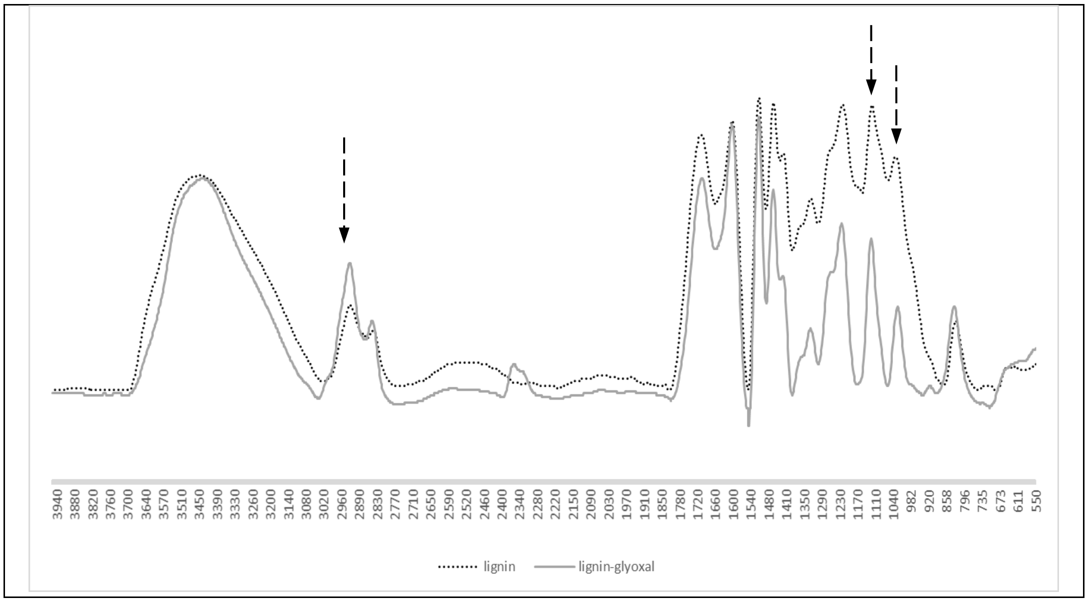

Fig. 1. FTIR spectra of soda lignin

Mechanical properties

The analysis of variance (ANOVA) of mechanical properties (MOE, MOR, and shear strength) of plywood is given in Table 2. Duncan's grouping of mechanical properties of plywood are shown in Figs. 2 to 4.

Table 2. Analysis of Variance (ANOVA) of Mechanical Properties of Plywood

		Shear strength			
Source	Sum of Squares	df	Mean Square	F	Sig.
Adhesive (A)	23.64	2	11.82	2.84	0.06
Adhesive amount (B)	4.25	2	2.12	0.51	0.60
A×B	1.54	4	0.38	0.09	0.98
		MOE			
Source	Sum of Squares	df	Mean Square	F	Sig.
Adhesive (A)	19069382.30	2	953491.14	0.33	0.71
Fiber orientation(B)	23404970.03	2	11702485.01	0.41	0.66
A×B	1193707.22	4	298426.80	0.01	1.00
		MOR			
Source	Sum of Squares	df	Mean Square	F	Sig.
Adhesive (A)	4762	2	2381	2.29	0.11
Fiber orientation(B)	1077	2	538	0.51	0.59
A×B	603	4	150	0.14	0.96

Shear Strength

The analysis of variance test indicated that the interaction and independent effects of the adhesive and its consumption amount were not significant. The highest plywood shear strength among the pure lignin (L.100%) and lignin-glyoxal adhesives belonged to the boards using lignin-glyoxal 30% (L.70%, G.30%) and the lowest belonged to the boards using pure lignin (L.100%). Additionally, the highest and the lowest shear strength of the produced plywood belonged to the adhesive usage amount of 160 gr/m^2 and 120 g/m^2, respectively (Figs. 2a - 2c). Environmental wood adhesives based on glyoxalated lignin were prepared and plywood with good mechanical properties (Wang *et al.* 2018).

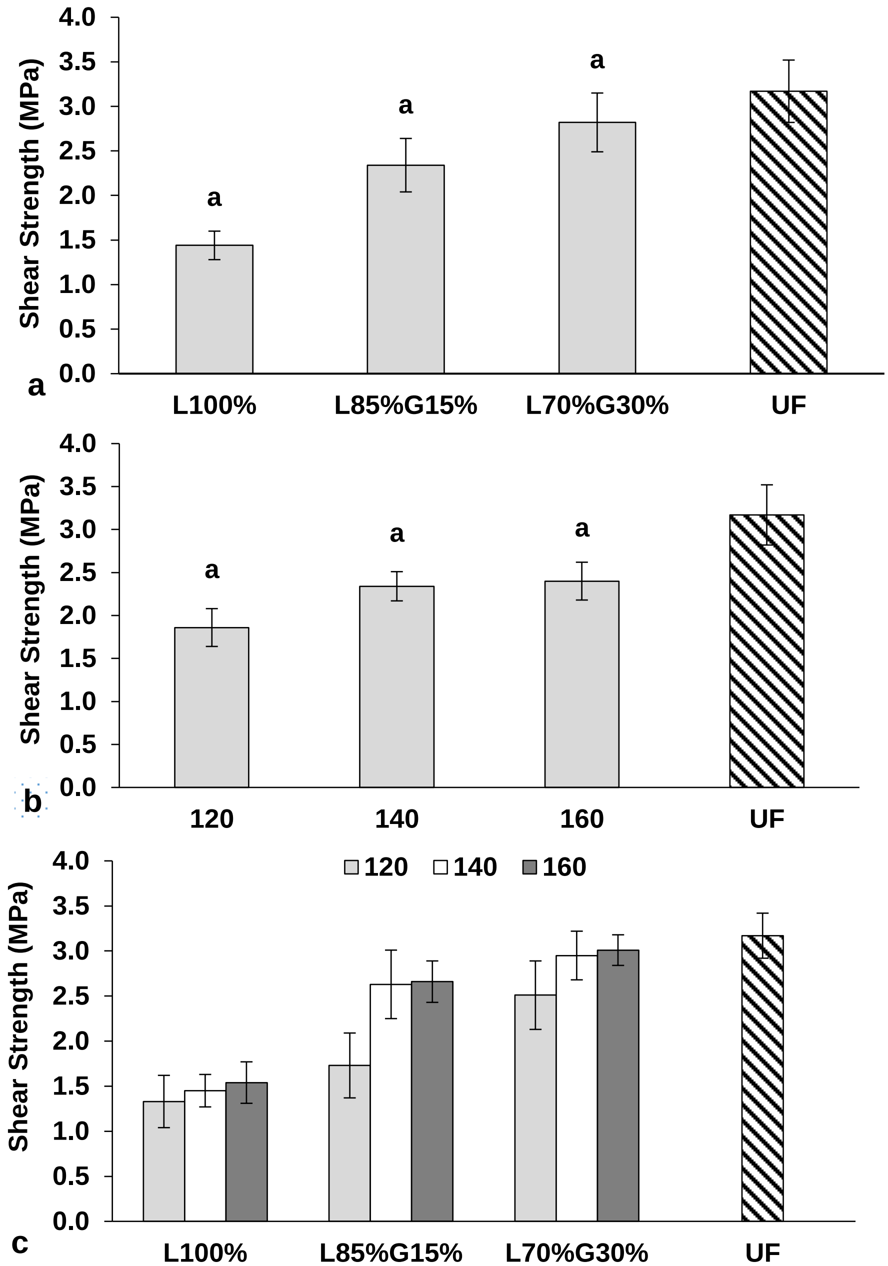

Fig. 2. a) Adhesive type, **b)** adhesive amount, and **c)** interaction and independent effects of adhesive and its consumption level on the shear strength of plywood

Modulus of Elasticity (MOE)

The variance analysis test indicated that the interaction and independent effects of the adhesive and its consumption amount were not significant. The highest plywood MOE among the pure lignin (L.100%) and lignin-glyoxal adhesives belonged to the boards using pure lignin (L.100%) and the lowest belonged to the boards using lignin-glyoxal 15% (L.85%, G.15%). Additionally, the highest and the lowest MOE of the produced plywood belonged to the adhesive usage of 160 g/m^2 and 120 g/m^2, respectively (Figs. 3a - 3c).

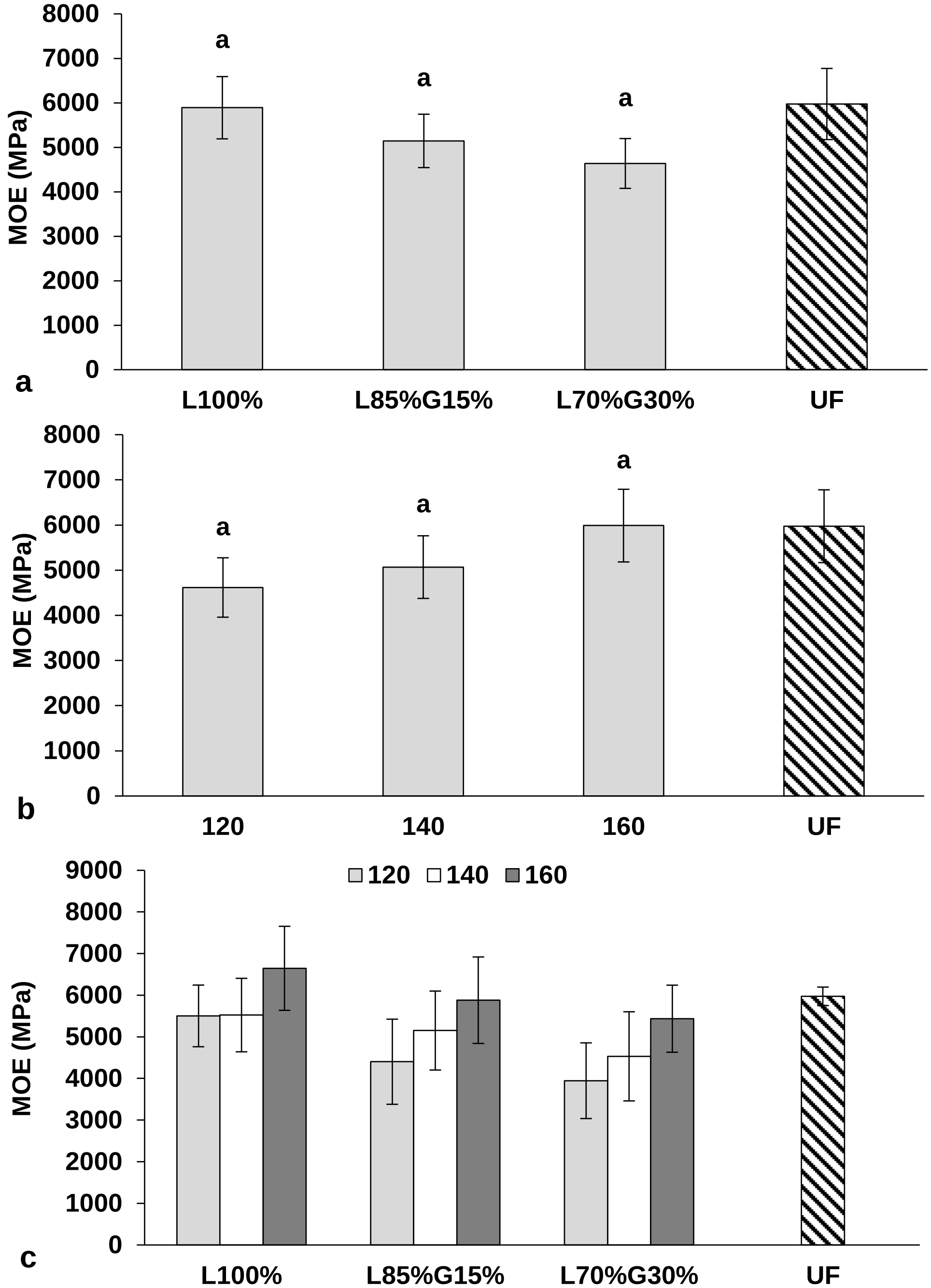

Fig. 3. a) Adhesive type, **b)** adhesive amount, and **c)** interaction and independent effects of adhesive and its consumption level on MOE of plywood

Modulus of Rupture (MOR)

The highest plywood MOR among the pure lignin (L.100%) and lignin-glyoxal adhesives belonged to the boards using lignin-glyoxal 30% (L.70%, G.30%) and the lowest belonged to the boards using pure lignin (L.100%). Additionally, the highest and the lowest MOR of the produced plywood belonged to the adhesive usage of 160 g/m^2 and 120 g/m^2, respectively (Figs. 4a-4c).

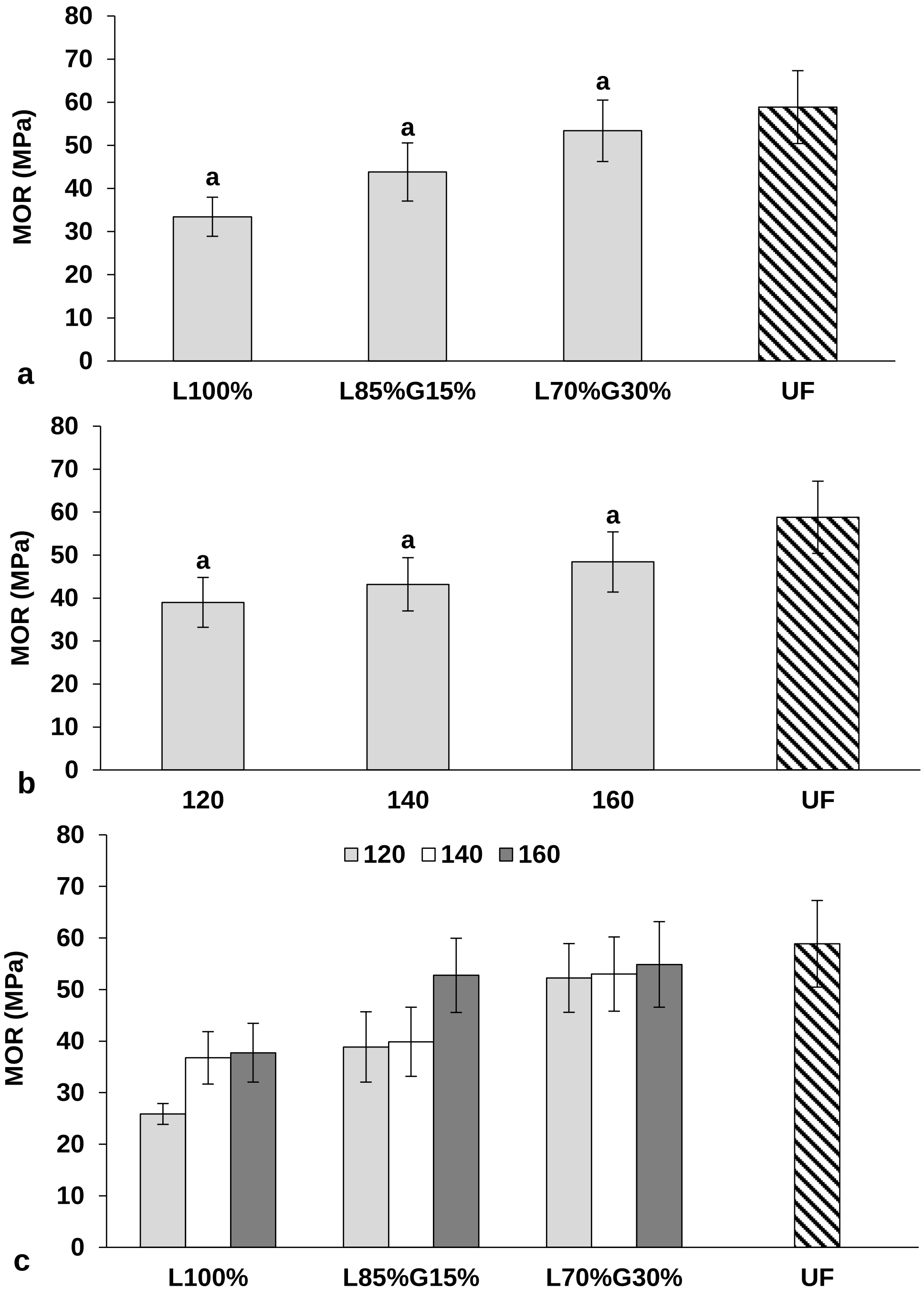

Fig. 4. a) Adhesive type, **b)** adhesive amount, and **c)** interaction and independent effects of adhesive and its consumption level on MOR of plywood

A comparison of the tensile properties of organosolv lignin formulations, which were impregenated and cured onto glass fiber paper strips, was made with those of PF resin. Organosolv lignin-based resins showed comparatively good strength and stiffness. The tensile strength properties of test samples made from organosolv lignin resins were equal to or better than those of test samples made from PF resin only (Sami Cetin and Ozmen 2003).

Physical Properties

The analysis of variance (ANOVA) of physical properties (thickness swelling at 2 and 24 h) of plywood is given in Table 3. Duncan's grouping of physical properties of plywood is shown in Figs. 5 and 6.

Table 3. Analysis of Variance (ANOVA) of Physical Properties of Plywood

Thickness swelling (2 h)	Sum of Squares	df	Mean Square	F	Sig.
Adhesive (A)	209.61	2	104.80	11.80	0.00
Adhesive amount (B)	16.15	2	8.07	0.91	0.41
A×B	8.54	4	2.13	0.24	0.91
Thickness swelling (24 h)	**Sum of Squares**	**df**	**Mean Square**	**F**	**Sig.**
Adhesive (A)	185.85	2	92.92	10.81	0.00
Adhesive amount (B)	16.27	2	8.13	0.94	0.40
A×B	8.16	4	2.04	0.23	0.91

The statistical analysis results indicated that the interaction and independent effects of the adhesive and its consumption amount on the shear strength, modulus of rupture, and modulus of elasticity were not significant. Among the pure lignin adhesives and those modified with glyoxal, only the lignin-glyoxal 30% (L.70%, G.30%) adhesive was most similar to the control adhesive for a majority of the tests. Meanwhile, these features in the control adhesive were better than those of the produced adhesives due to the better physical and chemical properties of the urea-formaldehyde adhesive than the natural lignin-glyoxal adhesive, as well as the better reactionary trend of formaldehyde than glyoxal. Additionally, the aromatic nucleus of lignin has less reactivity than formaldehyde, as it has less free space and the methoxy groups in the aromatic lignin rings are less reactive than the hydroxyl groups (Younesi-Kord Khalili and Honarbakhsh-Raof 2015c). These findings conform with the research results of Younesi-Kord Khalili *et al*. (2015a) and El Mansouri *et al*. (2007b).

Thickness Swelling (TS)

A variance analysis indicated that the independent effect of the adhesive on the thickness swelling of plywood after 2 and 24 h immersion in water was significant. The Duncan’s table classified the average thickness swelling of plywood using lignin-glyoxal 30% (L.70%, G.30%) and pure lignin (L.100%) into one group and the plywood using lignin-glyoxal 15% (L.85%, G.15%) into another group. Moreover, the independent influence of the usage amount and the mutual effect of type and usage amount were not significant.

The highest value of plywood thickness swelling after 2 and 24 h of immersion in water belonged to boards using the lignin-glyoxal 15% (L. 85%, G.15%) adhesive and the lowest value belonged to the boards using the lignin-glyoxal 30% (L.70%, G.30%) adhesive. Additionally, the highest and lowest value of plywood thickness swelling after 2 and 24 h of immersion in water belonged to the boards made using 120 and 160 g/m^2 adhesive, respectively (Figs. 5 and 6).

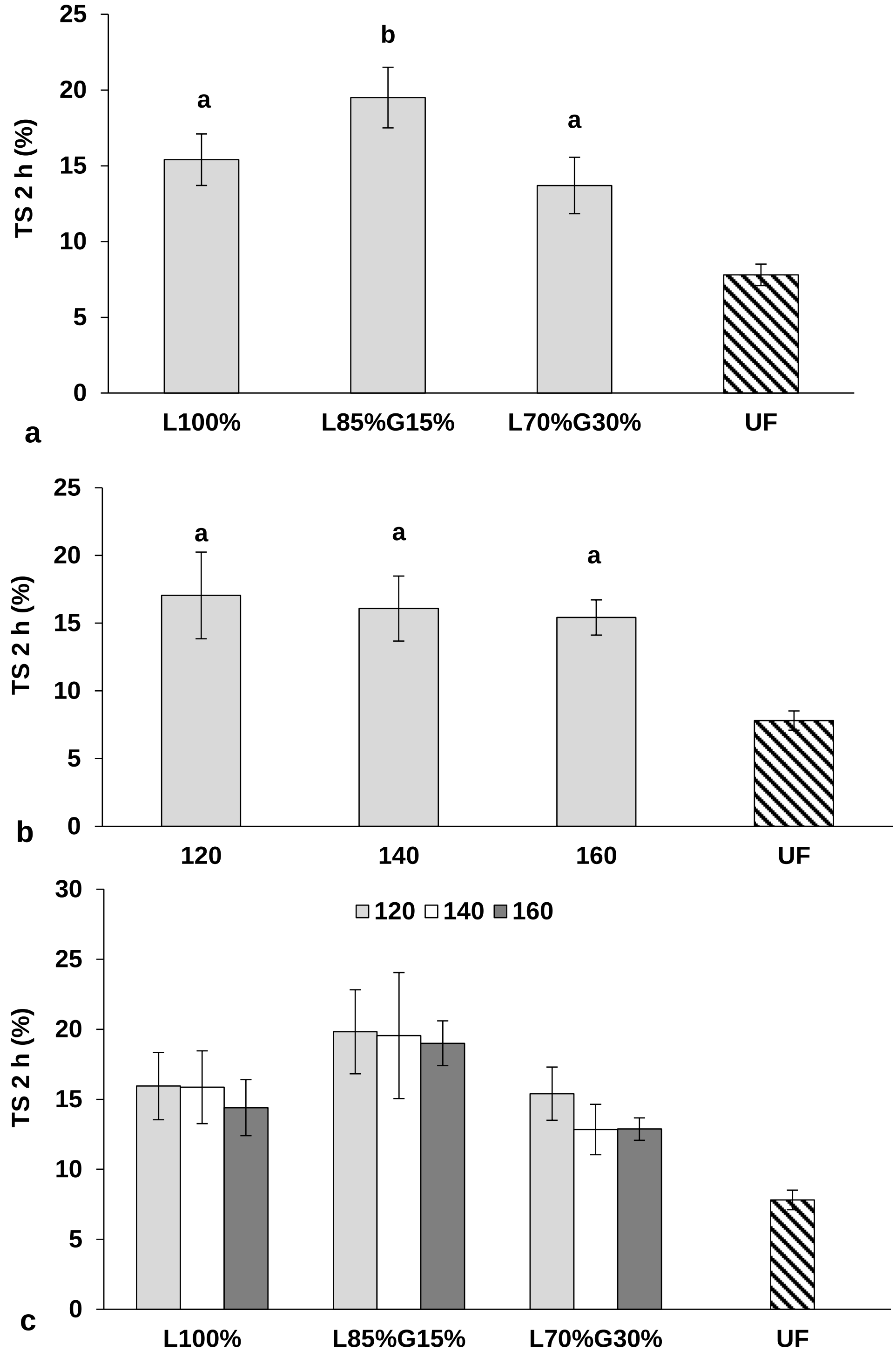

Fig. 5. a) Adhesive type, **b)** adhesive amount, and **c)** interaction and independent effects of adhesive and its consumption level on thickness swelling after 2 h immersion in water

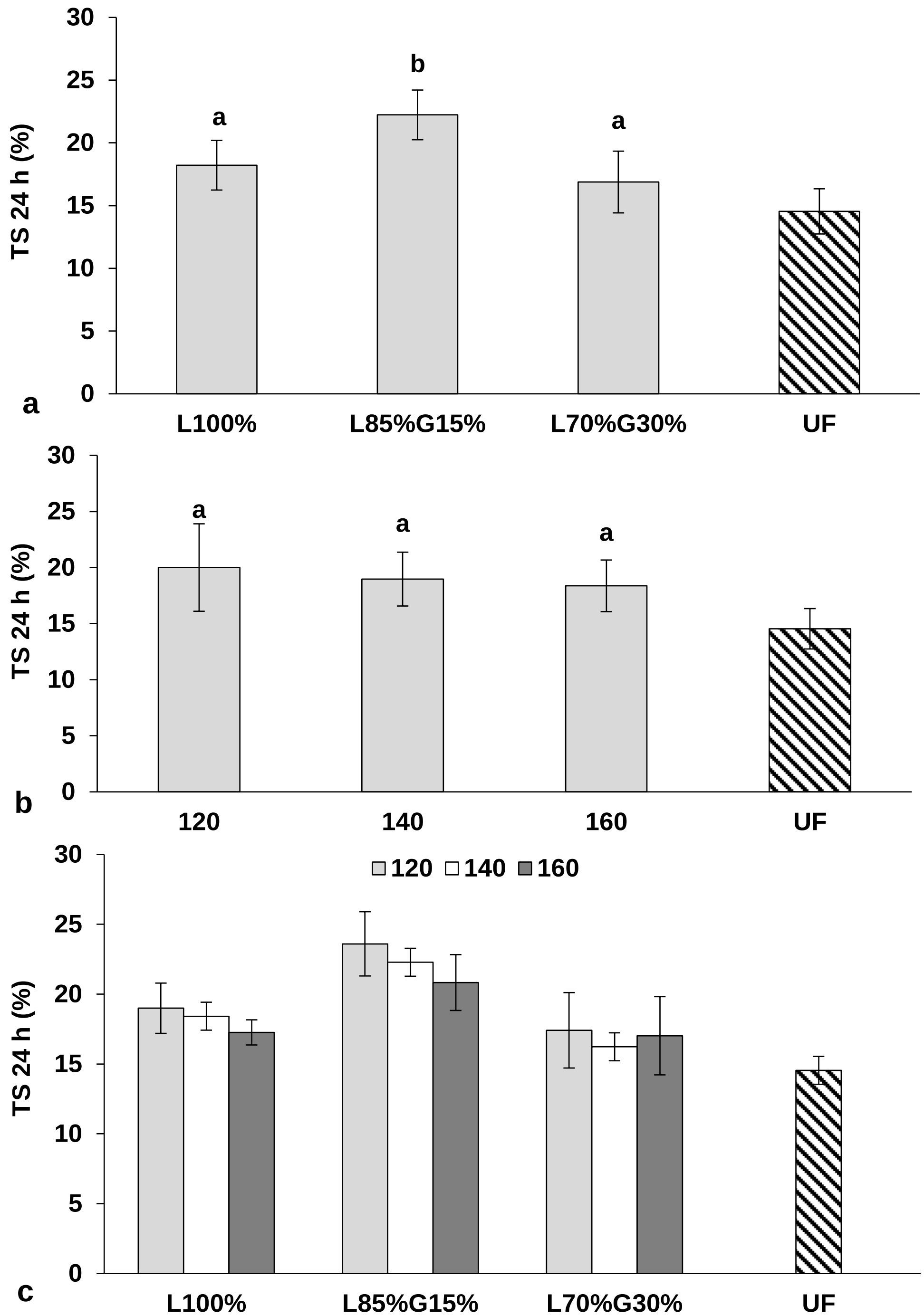

Fig. 6. a) Adhesive type, **b)** adhesive amount, and **c)** interaction and independent effects of adhesive and its consumption level on thickness swelling after 24 h immersion in water

The independent effect of the adhesive type on the plywood's physical properties (thickness swelling) was statistically significant. The least thickness swelling in the produced adhesives of pure lignin and lignin-glyoxal belonged to the boards using lignin-glyoxal 30% (L.70%, G.30%). Lignin glyoxalization significantly reduced the thickness swelling in the boards made with the lignin adhesive as it increased the reaction sites in the glyoxalized lignin molecules (Younesi-Kord Khalili *et al*. 2015b). The thickness swelling in the boards with the control adhesive was still far lower (better) than the boards produced with natural adhesives, which was in agreement with the research results of Jamalirad *et al.* (2007). The results also showed that the independent influence of the adhesive amount in the experiment boards with different adhesives was not statistically significant. The optimal state belonged to the boards using 160 g/m^2. Rassam and Faezzipour (2004) found that when using lignin kraft fiber boards, a higher adhesive amout used resulted in improved fiberboards links as well as better and more connections that were made. As a result, the hygroscopic area decreased and the dimensional stability is improved (Rassam and Faezzipour 2004).

CONCLUSIONS

Following results have been achieved through present research:

1. FT-IR spectroscopy confirmed that the compared to the original lignin, the modified lignin was more reactive and can effectively be applied to wood adhesives or other composite biomass as raw materials.
2. Mechanical and physical properties of plywood increased with increased adhesive usage amount.
3. The best mechanical and physical properties of the plywood among the natural adhesives were associated with the lignin-glyoxal 30% (L.70, G.30) adhesive.
4. The adhesive type and change in the usage amount did not have a significant effect on the mechanical and physical properties of plywood.
5. Thickness swelling of plywood was significantly changed with the change of adhesive type.
6. The lignin-glyoxal 30% (L.70, G.30) adhesive was numerically the closest option to urea-formaldehyde adhesive.

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