Korean J. Chem. Eng., **25**(1), 134-138 (2008)

Optimization of adhesive strength to plywood of gelatin processed from dorsal skin of yellowfin tuna (*Thunnus albacares*)

Jae-Hwan Yoon, Jin-Wook Woo, Hye-Jin Rho, Ju-Ryun Ahn, Sung-Jae Yu, Yang-Bong Lee, Chang-Kwon Moon* and Seon-Bong Kim†

Department of Food Science and Technology/Institute of Food Science, and
*Department of Materials Science and Engineering, Pukyong National University, Busan 608-737, Korea
(*Received 6 April 2007 • accepted 10 June 2007*)

Abstract−Gelatin from yellowfin tuna (*Thunnus albacares*) dorsal skin was optimized for adhesive strength to plywood using surface response methodology of a central composite design with a dependent variable of adhesive strength (Y, kg_f/cm^2) and two independent variables of gelatin concentration (X_1, %) and hardening time (X_2, hrs). From the above design, a maximum adhesive strength of 49.84 kg_f/cm^2 was obtained under the optimal treatment condition of 15.85% gelatin concentration and 25.68 hr hardening time. The adhesive strength under optimum conditions was 50.93 kg_f/cm^2. The adhesive strength of the tuna gelatin was shown to be superior to that of bovine and porcine gelatins which had adhesive strengths of 34.75 and 34.9 kg_f/cm^2, respectively.

Key words: Yellowfin Tuna (*Thunnus albacares*), Gelatin, Adhesive Strength, Response Surface Methodology

INTRODUCTION

Adhesive has numerous uses and forms, but in all cases is a type of solvent-based adhesive with each kind having specific advantages in adhesive efficiency and capability. However, the use of solvent-based adhesives is controlled in countries such as Korea, Japan and in Europe because harmful solvents are used for processing. Glues are widely used in various human endeavors, with applications for small industries and hermetical architecture working places such as factories and workshops. Therefore, the use of solvent-based adhesives sometimes presents human health hazards due to solvent vapors in poorly ventilated areas [1]. Some solvents are also known to be environmental hazards and are regulated to reduce air and water contamination.

Such volatile organic compounds as benzene, toluene, xylene, styrene and aldehydes used in wallpapers and paint, household furniture or in building materials in new apartment and multiplex facilities are known to be very harmful to humans, and are believed to adversely affect air quality and health. Therefore, concern for the development of environmentally safe materials such as natural/harmless adhesives and natural pigments has increased, and the production of environmentally safe adhesives using solvent-free adhesives is a high a priority [2].

Researches on environmentally safe solvent-free adhesives such as hotmelt adhesives, photocurable adhesives and water-based adhesives [3,4] have been carried out. Among them, the studies using domestic natural resources include ultrafiltration and adhesive characteristics of alkali-soluble extracts from Radiata pine barks [5], preparation of biological adhesives from chitosan by chemical modification [6], and adhesion properties of fish glue [2]. Little research on tuna dorsal skin gelatin has been done.

This study evaluated the physical adhesion properties of gelatin, which is known to be an adhesive and is used for attaching wood and mother of pearl. Mammalian-derived adhesive is made from boiling animal skin or bones producing a yellowish brown natural glue. Though it is similar to fish glue, the yield is higher, its bonding is superior and it has little smell.

Fish gelatin adhesives also have the disadvantage of moisture instability, but have the health and environmental advantages of no heavy metals or harmful volatile organic compounds and auto-degradability [7]. Bovine and porcine gelatins, which are used commercially, sharply increased in production as functional properties of the gelatins progressed. Recently, they are also under review for other practical applications such as sealants and hemostatic aids [8].

However, the mammalian gelatins have a safety problem because of bovine spongiform encephalopathy (BSE) and foot/mouth disease [9]. As a replacement for the mammalian resources, gelatins obtained from byproducts of fish processing have been actively studied [10]. For the processing of fish gelatins, Alaska Pollack [11], lumpfish [12], tilapia [13], conger and squid [14], codfish, hake, and sole [15] have been studied. However, the physical properties of the gelatins obtained from byproducts of fish processing were inferior to those of mammalian gelatins, with little commercial value [16]. Cho et al. [16] reported that some physicochemical properties of yellowfin tuna dorsal skin gelatin are superior to bovine and porcine gelatins. Therefore, the objectives of this study were to optimize such treatment conditions as gelatin concentration and hardening time to obtain the greatest adhesive strength to plywood by response surface methodology by using the dorsal skin gelatin of yellowfin tuna, and to investigate the functional properties of the tuna gelatin as a replacement for bovine and porcine gelatins to obtain more environmentally friendly and safe adhesives.

EXPERIMENTAL

1. Materials

Yellowfin tuna (*T. albacares*) skin was provided as frozen state

†To whom correspondence should be addressed.
E-mail: owlkim@pknu.ac.kr

from Dooyoung Fisheries Co., LTD (Busan, Korea) in January, 2006. The yellowfin tuna skin was separated into abdominal and dorsal skins; the dorsal skin of yellowfin tuna was used to extract gelatin according to the method of Cho et al. [16]. The extracted gelatin was tested for its usefulness as a kind of glue. For testing adhesive strength, Lauan hardwood plywood (1,220×2,440×2.7 mm) was purchased by selecting a wood with consistent grain quality. The wood was cut into 2.5×10×0.27 cm blocks and stabilized for 1 week at 20±1 ºC and RH 45±9%. For comparison with other animal gelatins, bovine gelatin (EC No 232-554-6, Type B) and porcine skin gelatin (EC No 232-554-6, Type A) were purchased from Sigma Chemical Co. (USA). All other chemicals used in this study were analytical grade.

2. Experimental Design for Optimization of Adhesive Strength of Gelatin from Dorsal Skin of Yellowfin Tuna

The experimental design for optimizing the adhesive strength of gelatin from dorsal skin of yellowfin tuna by varying gelatin concentration and hardening time was carried out by using a central composite design (CCD, Box & Wilson, 1951) [17] which had centers and ranges of two independent variables fixed from preliminary results (Table 1). For the central composite design, gelatin concentration had five points of 7.85, 10, 15, 20, 22.15%, and hardening time also had five points of 6.84, 12, 24, 36, 41.16 hr, with central points of 15% and 24 hr, respectively. The central composite design had 4 factorial points, 4 axial points (α=1.43) and 3 central points, having total 11 experimental points (Table 2). Multiple regression analysis on the surface response method was done by using SAS software (Version 8.01, SAS Institute Inc., USA). The model equation for gelatin adhesive strength (Y, kg_f/cm^2) as the dependent variable was shown with two independent variables of gelatin concentration (X_1, %) and hardening time (X_2, hrs).

Table 1. Experimental ranges and values of the independent variables in the central composite design for adhesive strength of gelatin from dorsal skin of yellowfin tuna (*Thunnus albacares*)

Independent variable	Symbol	Range and level				
		−1.43	−1	0	+1	+1.43
Gelatin concentration (%)	X_1	7.85	10	15	20	22.15
Hardening time (hr)	X_2	6.84	12	24	36	41.16

Table 2. Central composite design and responses of the dependent variables for adhesive strength of gelatin from dorsal skin of yellowfin tuna (*Thunnus albacares*) to the independent variables

Run no.	Coded level of variables		Response
	X_1	X_2	Y
1	10	12	31.35
2	20	12	38.43
3	10	36	38.91
4	20	36	40.22
5	7.85	24	26.23
6	22.15	24	37.59
7	15	6.84	39.45
8	15	41.16	41.18
9	15	24	48.61
10	15	24	48.86
11	15	24	80.93

X_1 (concentration of gelatin, %), X_2 (hardening time, hr). Y (adhesive strength, kgf/cm^2)

The model equation for the surface response method was obtained by using SAS software (Version 8.01, SAS Institute Inc.) of RSREG procedure with a confidence level of 99%, based on the following formula (1).

$$Y = \beta_0 + \sum_{i=1}^{4}\beta_i X_i + \sum_{i=1}^{4}\beta_{ii} X_i^2 + \sum_{i=1}^{3}\sum_{j=i+1}^{4}\beta_{ij} X_i X_j \quad (1)$$

where Y is dependent variable for gelatin adhesive strength (Y, kg_f/cm^2), β_0, β_i, β_{ii}, β_{ij} are regression coefficients and X_i, X_j are independent variables.

Based on the model equation obtained from formula (1) and the results of Table 2, a three-dimensional response surface plot was drawn by using Maple software (Maple 7. Waterloo Maple Inc., Canada) to facilitate visualization of effects of the two independent variables on the dependent variable.

3. Lap Shear Test of Gelatins

The different concentrations of gelatin were melted for 30 min in a water bath of 60 ºC, and 0.08 g of gelatin was applied onto a 2.5×1.25 cm area of the surface of the 2.5×10×0.27 cm wood sample. A force of 490,000 N/m^2 was applied for 10 min to the attached wood sample. Afterwards, the samples were placed in an incubator for the duration of the specified hardening times at 22±1 ºC, RH 50±1%. The adhesive strength was measured with a universal test machine (Testometric micro350, UK) at the rate of 5 mm/min for lap shear test [18]. For comparisons of adhesive strengths with mammalian gelatins, the same independent variables as the optimum conditions for dorsal skin gelatin from yellowfin tuna (*Thunnus albacares*) were applied to mammalian gelatins. Five replications were performed for all samples.

4. Statistical Analysis

The significant difference of experimental design data was represented by the analysis of variance (ANOVA) of SAS program at the probability level of α=0.05.

RESULTS AND DISCUSSION

The optimum conditions for maximizing adhesive strength of gelatin were investigated by using the RSREG (response surface regression) procedure of SAS (Version 8.01, SAS Institute Inc., U.S.A.). Based on the preliminary results, the independent variables were chosen and their ranges for the central composite design were fitted well as shown in Table 1. A total of 11 experimental points of the four factorial points, 4 (α=1.43) axial points and 3 central points were randomly designed to reduce statistical errors (Table 2). A fitted response surface model equation on gelatin adhesive strength was obtained by using the SAS system of RSREG procedure on the response surface methodology. The p-values of the terms of X_2 and X_1X_2 were higher than 0.05, so the significance level was low. Therefore, after the terms of low significance levels were removed, the model equation on gelatin adhesive strength was obtained by the terms (X_1, X_1^2, X_2^2) with high significance levels at p-value <0.05.

Table 3. Estimated coefficients of the fitted quadratic polynomial equation for the response of Y (adhesive strength, kg_f/cm^2) based on t-statistic

Parameter	Estimated coefficient	Standard error	*T*-value	*p*-value
Intercept	49.4790	1.0892	45.43	<.001
X_1[a]	3.0452	0.6634	4.59	0.0059
X_2[b]	1.4616	0.6634	2.20	0.0789
X_1X_1	−8.3908	0.7820	−10.73	0.0001
X_1X_2	−1.4425	0.9434	−1.53	0.1868
X_2X_2	−4.2806	0.7820	−5.47	0.0028

[a]X_1 (concentration of gelatin, %).
[b]X_2 (hardening time, hr).

Table 4. Analysis of variance (ANOVA) for the response of the dependent variable (Y, adhesive strength)

Sources	DF[a]	SS[b]	MS[c]	*F*-value	*p*-value
Regression					
Linear	2	92.30	49.15	12.96	0.0105
Quadratic	2	429.03	214.52	60.26	0.0003
Cross-product	1	8.32	8.32	2.34	0.1868
Model	5	529.66	271.99	29.76	0.0010
Residual					
Lack of fit	3	14.56	4.85	2.99	0.2605
Pure error	2	3.24	1.62	-	-
Total error	5	17.80	3.56	-	-
Total	10	547.46	275.55	-	-

[a]DF (Degrees of Freedom).
[b]SS (Sum of Square).
[c]MS (Mean Square).

The model equation of surface response method is shown in the formula below (2).

$$Y=49.478959+3.045168X_1-8.390779X_1^2-4.280554X_2^2 \quad (2)$$

The determinant coefficient (R^2) for the above model equation was 0.9675 and its P-value was 0.001, showing significance at the level of over 99%. Also, the significance level of the independent variable of gelatin concentration (X_1, %) was a high value of 99.41%, but the significance level of hardening time (X_2, hr) was a low value of 92.11% (Table 3).

In the analysis of variance (ANOVA), the p-values of the linear and quadratic terms for the fitted regression were 0.0105 and 0.0003, respectively, showing high significance levels of 98.95% and 99.97%. However, the significance level of the cross-product (X_1X_2) was a low value at 81.32%. The total model was highly significant at 99.9% (Table 4).

Table 6. Experimental and predicted results of verification under the optimized condition

Item	Y (Dependent variable, adhesive strength, kg_f/cm^2)
Predicted value	49.84
Experimental value	50.93

Optimized condition: 15.85% gelatin concentration and 25.68 hr hardening time.

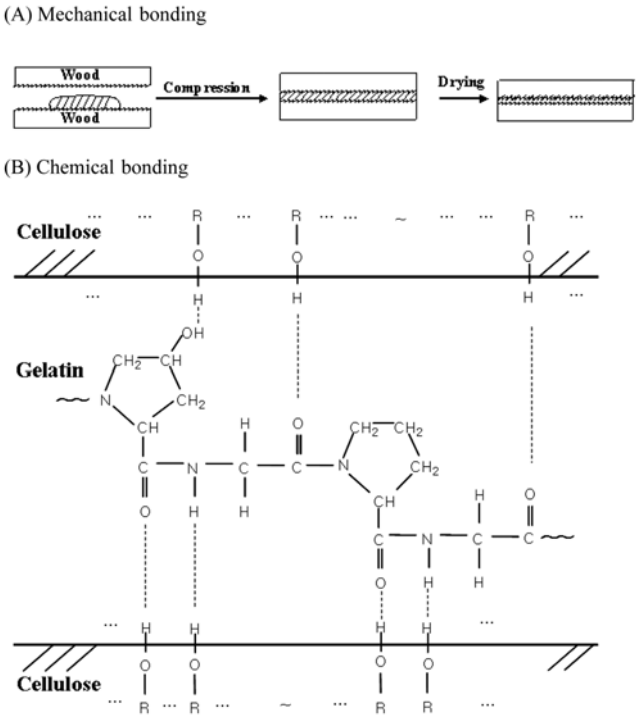

Fig. 1. Simplified diagram of bonding formation by mechanical (A) and chemical (B) reaction between gelatin and cellulose.

The highest adhesive strength of the gelatin was obtained with 15.85% gelatin concentration and 25.68 hr hardening time (Table 5). Under optimum conditions, the predicted value was 49.84 kgf/cm^2 and the experimental value was 50.93 kgf/cm^2, showing little difference, even though it was a slightly higher value. The experimental value realized was 102.2% of the predicted value, demonstrating the effectiveness of optimizing gelatin conditions on maximizing adhesive strength (Table 6). Fig. 1 is a simplified flow diagram of the procedure of bonding between gelatin and plywood, which is formed by physical forces and chemical reactions. Choi [19] reported three types of bonding mechanisms: mechanical bonding, chemical bond-

Table 5. Optimal conditions for maximizing adhesive strength of gelatin from dorsal skin of yellowfin tuna (*Thunnus albacares*)

Dependent variables	Independent variables	Critical value		Predicted value	Stationary point
		Coded	Uncoded		
Y	X_1	0.17	15.85	49.84	50.93
	X_2	0.14	25.68		

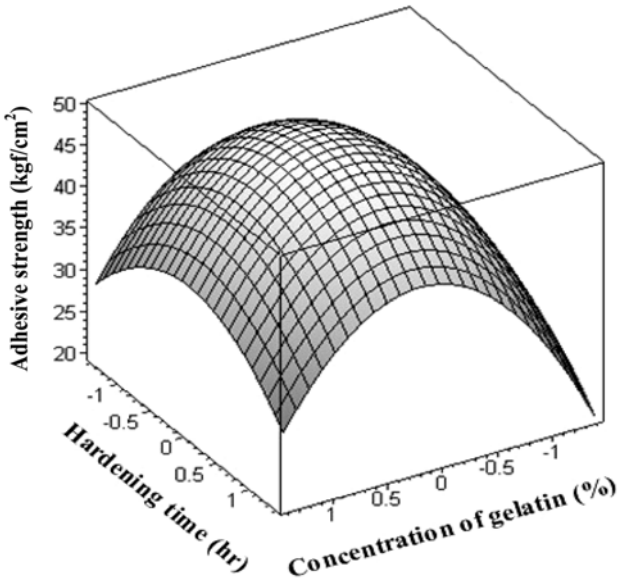

Fig. 2. Response surface plot for optimization of adhesive strength of gelatin from dorsal skin of yellowfin tuna (*Thunnus albacares*).

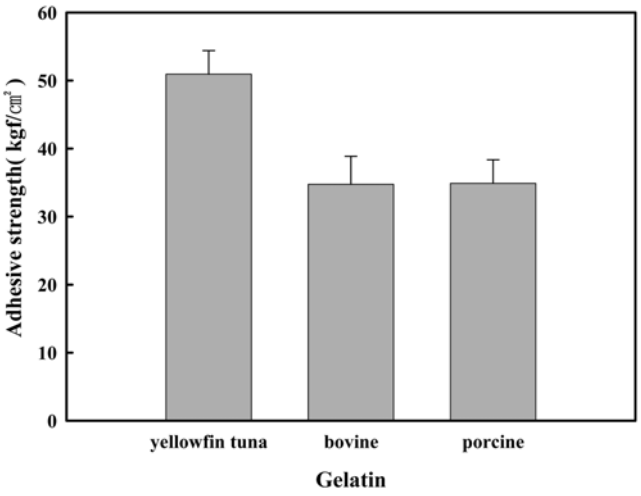

Fig. 3. Comparisons of adhesive strength of yellowfin tuna, bovine and porcine gelatins. The maturation was done at 22±1 ºC for 25.68 hrs.

ing and attracting forces. Mechanical bonding and chemical bonding are formed by flowing glue into micropores of adherening and hardening forming by attracting forces between molecules of adhesive and adherend, respectively [19]. Even though the surface of adherend is smooth, the surface is still rough when observed more closely. When gelatin is applied to plywood, gelatin fluidity causes it to flow into the lower areas of the rough surface. During hardening, the surface becomes smoother and the adhesive strength is improved. Furthermore, reactive portions in gelatin molecules form chemical bonds resulting from van der Waals forces and hydrogen bonding, increasing the adhesive strength [19].

Three-dimensional response surface plots of the dependent variable (Y, kg_f/cm^2) of adhesive strength and the independent variables of gelatin concentration (X_1, %) and hardening time (X_2, hr) were drawn by using Maple software (Maple 7. Waterloo Maple Inc., Canada) and shown in Fig. 2. Two important determinants of adhesive strength are gelatin concentration (%) and hardening time (hr). Gelatin adhesive strength (kg_f/cm^2), the dependent variable, was increased up to the highest value as the coded values for two independent variables of gelatin concentration (%) and hardening time (hr) were near to 0 values. The adhesive strength of the gelatin increased as the gelatin concentration increased from 7.93% to 15.85%, but it decreased as gelatin concentrations exceeded 15.85%. The adhesive strength of the gelatin increased as the hardening time increased from 7.03 hours to 25.68 hours, but it decreased with more than 25.68 hardening hours.

The reason for the limits for gelatin concentration is believed to be that fluidity decreased and gel strength and viscoelasticity increased with gelatin concentration, so adhesive thickness increased and gelatin did not sufficiently flow into the uneven parts of the adherend. The postulated explanation for the limits of hardening time was that the adhesive strength decreased because internal stress was formed as hardening time increased [19,20].

In the comparisons of the effects of the two independent variables on adhesive strength (Y, kg_f/cm^2), hardening time (X_2, hr) had less of an effect than did gelatin concentration (X_1, %), in the range from 0 to −1 of coded values. Therefore, gelatin concentration (%) affected adhesive strength more than hardening time (hr).

In the comparisons with adhesive strengths of other animal gelatins, the adhesive strengths of bovine and porcine gelatins were 34.75 and 34.9 kg_f/cm^2, respectively. Therefore, the adhesive strength (50.93 kg_f/cm^2) of yellowfin tuna gelatin was superior to that of the other animal gelatins (Fig. 3), suggesting tuna gelatin may be a useful as a replacement for bovine or porcine gelatins in adhesives. Therefore, further studies are needed on the functional properties of gelatins obtained from fish skins to evaluate their usefulness in wider industrial applications.

ACKNOWLEDGMENTS

This work was supported by the Technical Development Program for Regional Industries (Grant No. 10024274) from the Ministry of Commerce, Industry and Energy, Korea.

REFERENCES

1. M. H. Park and J. H. Kim, *Polymer Sci. Technol.*, **6**, 595 (1995).
2. Y. K. Lee, H. D. Hwang and H. J. Kim, *Mokchae Konghak*, **32**, 56 (2004).
3. H. S. Do, Y. J. Park, S. M. Kim, D. H. Lim and H. J. Kim, *Prosp. Indust. Chem.*, **7**, 14 (2004).
4. M. C. Lee, M. C. Park and I. S. Seo, *Polym. Sci. Technol.*, **11**, 450 (2000).
5. N. S. Cho, *Mokchae Konghak*, **26**, 29 (1998).
6. K. D. Min, W. H. Park, D. I. Yoo and S. Hudson, *Textile Sci. Eng.*, **42**, 60 (2005).
7. D. C. Jeong, *Chem. World*, **37**, 40 (1997).
8. D. J. Chung and T. Matsuda, *J. Indust. Eng. Chem.*, **4**, 340 (1998).
9. S. M. Cho, K. S. Kwak, D. C. Park, Y. S. Gu, C. I. Ji, D. H. Jang, Y. B. Lee and S. B. Kim, *Food Hydrocol.*, **18**, 573 (2004).
10. M. Gudmundsson, *J. Food Sci.*, **67**, 2172 (2002).

11. S. K. Kim, H. G. Byun and E. H. Lee, *J. Korean Indust. Eng. Chem.*, **5**, 547 (1994).
12. K. Osborne, M. N. Voight and D. E. Hall, Lancaster, PA, *Advances in fisheries technology and biotechnology for increased profitability*, Technomic Publishing Co, 143-153 (1990).
13. B. Jamilah and K. G. Harvinder, *Food Chem.*, **77**, 81 (2002).
14. J. S. Kim and S. Y. Cho, *Agric. Chem. Biotechnol.*, **39**, 134 (1996).
15. M. C. Gómez-Guillén, J. Turnay, M. D. Fernández-Díaz, N. Ulmo, M. A. Lizaebe and P. Montero, *Food Hydrocol.*, **16**, 25 (2002).
16. S. M. Cho, Y. S. Gu and S. B. Kim, *Food Hydrocol.*, **19**, 221 (2005).
17. I. M. Edwards and A. Jutan, *Comp. Chem. Eng.*, **21**, 441 (1997).
18. *American Society of Testing Materials*, Standard test method for apparent shear strength of lap joint adhesively bonded metal specimens by tension loading (1995).
19. S. Y. Choi, *Korean Inst. Rub. Indust*., **25**, 291 (1990).
20. J. S. Kim, S. Y. Choi, J. H. Ha and E. H. Lee, *Korean J. Food Sci. Technol.*, **27**, 483 (1995).