ORIGINAL ARTICLE

Effects of phenol-formaldehyde / isocyanate hybrid adhesives on properties of oriented strand lumber (OSL) from rubberwood waste

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Abstract

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The objective of this research project was to study the effects of hybrid adhesives of Phenol-Formaldehyde (PF) and Polymeric Diphenylmethane Diisocyanate (MDI) on the properties of Oriented Strand Lumber (OSL) to determine the optimal ratio of both adhesives. The results showed that OSL formed by pure adhesive or hybrid adhesives (3 blends: 25:75, 50:50 and 75:25) had properties that pass the CSA O437.1 standards, such as (1) modulus of rupture, (2) modulus of elasticity, and (3) internal bond strength. However, the thickness swelling and bond durability of OSL formed by pure MDI failed to pass the standards, while those formed by pure PF or hybrid adhesives passed. Among the three blends of adhesives, the blend 75:25 (PF: MDI) gave the best properties while ratio of 50:50 gave the worst properties, especially internal bond strength due to the phase separation of both adhesives. In addition, the modulus of rupture

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and modulus of elasticity in the "edgewise" direction were higher than those in the "flatwise" direction. In the edgewise direction, load is transferred in the direction of width of strand that is large while in the flatwise direction, load is transferred in the direction of thickness of strand which is small.

Key words : oriented strand lumber, rubberwood, phenol-formaldehyde, isocyanate adhesive

บทคัดย่อ

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ผลของกาวผสมฟีนอลฟอร์มัลดีไฮด์/ไอโซไซยาเนตต่อสมบัติของแผ่นแถบไม้เรียงเสี้ยนที่ได้จากเศษไม้ยางพารา

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งานวิจัยนี้ศึกษาเปรียบเทียบผลของกาวผสมระหว่างฟีนอลฟอร์มัลดีไฮด์ (Phenol-Formaldehyde, PF) กับกาวไดฟีนิลมีเทน ไดไอโซไซยาเนต (Polymeric Diphenylmethane Diisocyanate, MDI) ต่อสมบัติของแผ่นแถบไม้เรียงเสี้ยน (Oriented Strand Lumber) เพื่อหาส่วนผสมที่ได้สมบัติที่ดีขึ้น ผลการทดลองพบว่า กาว PF กาว MDI และกาวผสม (3 สูตร ได้แก่ 25:75, 50:50 และ 75:25) มีค่าสมบัติเกือบทุกชนิดสูงกว่าค่ามาตรฐาน CSA O437.1 ได้แก่ (1) โมดูลัสของการแตกหัก (2) โมดูลัสของความยืดหยุ่น และ (3) ความแข็งแรงของการยึดติดภายใน ยกเว้นการพองตัวทางด้านความหนาและความทนทานของการยึดติดของแผ่นแถบไม้เรียงเสี้ยนที่เตรียมโดยกาว MDI 100% ไม่ผ่านมาตรฐาน ในขณะที่กาว PF 100% และกาวผสม PF:MDI เกือบทุกอัตราส่วนผ่านมาตรฐาน สำหรับกาวผสมทั้งสามสูตร พบว่า กาวผสม PF: MDI ที่อัตราส่วน 75:25 ให้สมบัติดีที่สุด ในขณะที่กาวผสม PF: MDI ที่อัตราส่วน 50:50 มีสมบัติที่ด้อยที่สุดโดยเฉพาะค่าความแข็งแรงของการยึดติดภายในเนื่องจากกาวทั้งสองแยกเฟสกัน นอกจากนี้ยังพบว่าค่าโมดูลัสของการแตกหัก และโมดูลัสของความยืดหยุ่นในการทดสอบด้านขอบมีค่าสูงกว่าในด้านระนาบของแผ่นไม้เรียงเสี้ยน ทั้งนี้เนื่องจากการรับแรงในด้านขอบจะมีการส่งแรงผ่านความกว้างของแถบไม้ซึ่งมีค่าสูง ในขณะที่การทดสอบด้านระนาบมีการส่งผ่านแรงตามความหนาของแถบไม้ซึ่งมีค่าต่ำ

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During rubberwood processing, there is a lot of waste, particularly small pieces, which can be used as a supply for Oriented Strand Lumber (OSL) production. OSL is a high strength wood composite produced from strands of wood that are aligned in the same direction and bonded by adhesives. The strand length is usually about 75-140 times its thickness. By making OSL, one obtains a structural material with high strength (Haygreen and Bowyer, 1989) and reduces waste.

It is extremely important to adhere all strands together so that the OSL possesses a high strength. Good adhesion is obtained when the cohesive strengths of the adhesive and wood, and the interfacial strength between them are high. There are many mechanisms of adhesion, such as mechanical interlocking, interdiffusion, adsorption, and chemical bonding (Gent and Hamed, 1990). For good adhesion, interphase is essential. Locus of failure may be categorized as

1. Cohesive failure in the wood which occurs when interfacial strength is high, and the adhesive layer is stronger than the wood.
2. Cohesive failure in the adhesive layer which takes place when the wood is strong but the adhesive layer is weak.
3. Interfacial separation or clean separation which occurs when adhesion between the wood

and adhesive is poor.

However, in some cases, mixed mode of cohesive failure and interfacial separation may be observed (Hamed, 2003). Two widely used adhesives in the wood industry are Phenol-Formaldehyde (PF) and Polymeric Diphenylmethane Diisocyanate (pMDI or MDI). The chemical structures of both adhesives are shown in Figures 1 and 2, respectively.

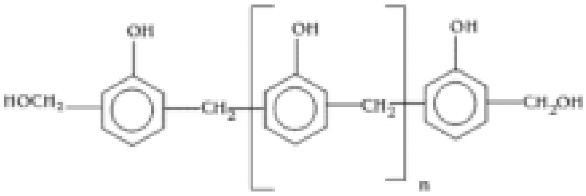


Figure 1. Structure of Phenol-Formaldehyde (PF) adhesive.

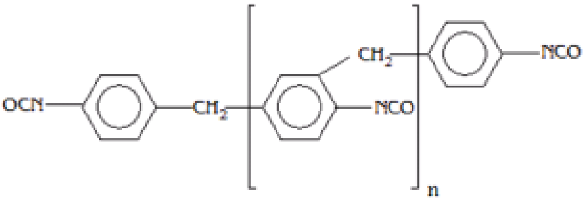


Figure 2. Structure of Polymeric Diphenylmethane Diisocyanate (MDI) adhesive.

PF adhesive is a thermoset polymer. It can exhibit hydrogen bonding and mechanical interlocking with wood (Schmidt, 1998). There are two types of PF resins, namely Novolak and Resole (Frihart, 2005):

- Novolak resins have formaldehyde to phenol ratios of 0.5-0.8 at a pH of 4 to 7. However, Novolak oligomers are not used as wood adhesives due to their low water solubility and high acidity.
- Resole resins have formaldehyde to phenol ratios of 1.0-3.0 at a pH of 7 to 13. Under basic conditions, addition of formaldehyde to phenol is fast, but conversion to the oligomer is slow. Thus heating is often necessary to obtain the final polymer or adhesive. Resole resin is used as wood adhesive.

MDI has low viscosity and low polarity, so it can penetrate into the wood very rapidly. The polymerization is fast and bonds form even in the presence of water. MDI can form strong bonds with other materials such as metal caul plate, and is promoted as a "formaldehyde-free adhesive". However, its high cost is a disadvantage (Frazier, 2003).

The objectives of this work are:

1. To study properties of OSL formed by PF and MDI adhesives
2. To determine the best ratio of adhesive blends.

Materials and Methods

Adhesives

Two types of adhesives were studied, Polymeric Diphenylmethane Diisocyanate (MDI) or Isocyanate adhesive, and Phenol-Formaldehyde (PF) adhesive. Hybrid adhesives were made by mixing both adhesives at a ratio of 75:25, 50:50, and 25:75 in a beaker and stirred with a stirring rod. Overall, two types of pure adhesives and three blends of adhesives were studied in this work. Properties of both adhesives are in Table 1.

Strand Preparation

Rubberwood waste was obtained from a rubber tree plantation in Nakhon Si Thammarat Province, Thailand. The left-over branches having a diameter of not more than 150 mm were

Table 1. Properties of Isocyanate and Phenol-Formaldehyde adhesives.

Property	Phenol-Formaldehyde PF-101	Isocyanate Atac 900 10
Viscosity (cps)	40-110	8,000-10,000
Solid content (%)	44±1	43±1
pH	11-13	6-7

transported to the laboratory and subsequently cut to a length of 140 mm. After removing the bark, the 140-mm branches were cut into strands using a CAE 6/36 Laboratory Disc Flaker at a disc speed of 990 rpm. The resulting branches had a diameter in range of 6.5-12.1 cm and a density of 0.45- 0.63 g/cm^3.

OSL Manufacturing

The rubberwood strands were dried until the moisture content was 5% in a rotating drum dryer. Adhesive was sprayed onto the strands increasing the weight by 6% based on their oven-dried weight. Strands with adhesive were aligned in the same grain direction and then pressed using compression molding at 25 MPa and 180^{o}C for 7 minutes. Then the pressure was reduced by a half and heating was continued for another 10 minutes. The total heating time was 17 minutes, as suggested by the adhesive suppliers. The size of each OSL was 75 cm x 30 cm x 2 cm.

OSL Properties

Equilibrium Moisture Content (EMC), Specific Gravity (S_g) and other properties were determined according to ASTM and CSA standards (ASTM 2001, 2001; CSA 1993). Mechanical properties were tested using a Lloyd universal testing machine (UTM) Model LR 150K. There were 5 specimens in each test, and each test was repeated 3 times.

The Modulus of Rupture (MOR) and Modulus of Elasticity (MOE) were tested by using three point bending in both directions: flatwise and edgewise (Figure 3). The specimen width was 20 mm while the length was 18 times the width. The testing rate was 1.3 mm/min.

Internal Bond Strength (IB): samples were cut into 50 mm x 50 mm and adhered to metal rods with an epoxy adhesive. The testing rate was 1.6 mm/min. Load was recorded until the sample was broken.

Thickness Swelling (TS): the specimen size was 150 mm x 150 mm. Samples were immersed in water at 20^{o}C for 24 hours. The thicknesses of samples were measured before and after the immersion.

Bond Durability: specimens with same size as MOR were immersed in boiling water for 2 hours. Then cooled down in 20^{o}C water for 1 hour before MOR testing.

Morphology

After the samples were tested, the fractured surfaces were examined by a Carl Zeiss optical microscope model Axioskop2 MAT to determine the locus of fracture, and miscibility of the hybrid adhesives. Photos were taken by a digital camera (Sony DSC-P100). PF and MDI have different colors so one may determine the type of adhesive in the samples after fracture.

Table 2. Equilibrium moisture content (EMC), MOR and specific MOR for both flatwise and edgewise directions.

Composition		Flatwise			Edgewise		
PF (%)	MDI (%)	EMC (%)	MOR (MPa)	MOR/S_g (MPa)	EMC (%)	MOR (MPa)	MOR/S_g (MPa)
0	100	7	50±5	63±2	7	69±11	96±16
25	75	7	42±8	52±12	8	59±4	92±11
50	50	8	42±9	57±12	8	41±14	56±17
75	25	7	60±14	77±20	7	71±1	100±15
100	0	8	62±18	80±23	7	67±14	89±14
Standard			**> 12**			**> 29**	

Results and Discussion

Modulus of Rupture (MOR)

The modulus of rupture (MOR) is a measure of the strength of the OSL. The MOR were determined in two directions: perpendicular (flatwise) and parallel (edgewise) to the plane of the specimen. MOR, specific MOR (MOR/S_g) and EMC are shown in Table 2. The Statistical Analysis System (SAS) was used to analyze the data. The results showed that all properties are significantly different ($P>0.05$), except MOR.

In the flatwise direction, OSL adhered by pure PF has the highest modulus of rupture (62 MPa) while pure MDI gives the lower MOR (50 MPa). At composition ratio of 25:75 and 50:50, the MOR decreased to 42 MPa. This was the lowest MOR we obtained. However, for 75:25, the MOR is still as high as pure PF (60 MPa compared to 62 MPa). All MOR (42-62 MPa) are higher than the standard value of 12 MPa. If one considers the MOR per specific gravity, or specific MOR, the specific MOR of 75:25 PF:MDI and pure PF are the highest (77 and 80 MPa), while others are in range of 52-63 MPa.

However, in the edgewise direction, MOR of OSL adhered by MDI is much higher than its flatwise results (69 MPa compared to 50 MPa). The results show the same behavior as that noted above that upon adding 25% or 50% of PF to MDI, the MOR decreased. The 50:50 ratio gives the lowest MOR (41 MPa). However, at 75:25 PF:MDI, the MOR increased to 71 MPa that is about the same as pure PF (67 MPa). For specific MOR, the highest value (100 MPa) is obtained in 75:25 PF:MDI blend, while the lowest (56 MPa) is in 50:50 PF:MDI blend.

Modulus of Elasticity (MOE)

The results of the modulus of elasticity (MOE) or stiffness are shown in Table 3. The behavior of the MOE is similar to the MOR in Table 2. In a flatwise direction, pure PF gives a higher MOE than pure MDI (8,520 vs 8,013 MPa). For 25:75 and 50:50 PF:MDI, the MOE are much lower than pure PF and pure MDI. Again, the 75:25 PF:MDI gives about the same value as pure PF (7,796 MPa vs. 8,520 MPa). For specific MOE, values of 75:25 PF:MDI and pure PF are comparable (10,041 MPa and 11,048 MPa, respectively).

In the edgewise direction, pure MDI gives a slightly higher value than pure PF. However, statistically, they are not significantly different. The 50:50 PF:MDI gives the lowest MOE of 6,696 MPa while 75:25 PF:MDI gives the highest of 10,029 MPa. If one considers the specific MOE, the 75:25 PF:MDI gives the highest value (14,057 MPa).

Since the main function of the adhesive is to bind strands together, the adhesive has its own modulus and adhesion strength. One may think that OSL is a kind of composite material that is composed of two components: wood strand and adhesive (thermoset). If one applies the "rule of

Table 3. Equilibrium moisture content (EMC), MOE and specific MOE for both flatwise and edgewise directions.

Composition		**Flatwise**			**Edgewise**		
PF (%)	**MDI (%)**	**EMC (%)**	**MOR (MPa)**	**MOR/S_g (MPa)**	**EMC (%)**	**MOR (MPa)**	**MOR/S_g (MPa)**
0	100	7	8,013±139	10,220±645	7	9,606±800	13,108±1,224
25	75	7	6,437±1,126	7,914±584	8	8,710±351	13,647±1,119
50	50	8	6,787±264	9,314±686	8	6,696±785	9,184±592
75	25	7	7,796±875	10,041±839	7	10,029±171	14,057±2,104
100	0	8	8,520±1,149	11,048±2,159	7	9,297±1,022	12,295±1,343
Standard			**> 1,500**			**> 5,500**	

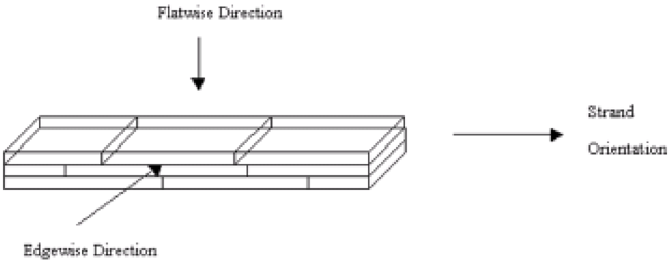


Figure 3. Directions of testing: flatwise and edgewise directions.

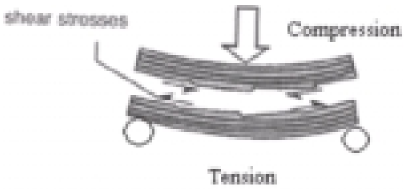


Figure 4. Shear force created in the sample during the three-point bending test.

mixture" to calculate the composite's modulus, it will not be much different since the weight percent of adhesive is only 6%.

MOE and MOR in the edgewise direction are larger than the flatwise direction. One may explain this by recalling that during the 3-point bending test, the sample was pressed at the middle. So the top of the OSL was subject to compression, while the bottom was subject to tension, and a shear force was created (see Figure 4). Since OSL is composed of a lot of strands bonded together by adhesive, the load is transferred from one strand to the adhesive, then to another strand. For testing in a flatwise direction, the load is applied to the strand in a direction where the thickness is small. On the other hand, in the edgewise direction, load is transferred in the direction of width which is much greater than the thickness (see Figure 3). Therefore the MOE and MOR in the edgewise direction are larger than those in flatwise direction.

Internal Bond Strength

In order to determine the adhesion strength, the internal bond strength test was performed. Results are shown in Table 4.

It is very obvious that PF gave a much higher internal bond strength than MDI (0.95 MPa compared to 0.54 MPa). The results showed the same tendency as MOR and MOE that the internal bond strength of the 50:50 blend is the lowest but the strength increased for the 75:25 PF: MDI blend. However, every blend of adhesive passed the standard CSA O437.1-93 that requires only 0.35 MPa. The reasons that PF has much higher adhesion are (Schmidt 1998, and Zheng, 2001) :

1. PF adheres to wood via hydrogen bonding better than MDI.

2. MDI molecules are larger than PF molecules so MDI requires more diffusion time. Thus, the hot pressing time of 17 minutes may not be sufficient for large molecules to diffuse and get some interphase.

Table 4. Internal bond strength (IB) of OSL.

Composition		Property		
PF	MDI	EMC	IB (MPa)	IB/S_g (MPa)
0	100	5	0.54±0.18	0.76±0.24
25	75	5	0.54±0.10	0.77±0.07
50	50	6	0.45±0.11	0.63±0.17
75	25	7	0.60±0.10	0.85±0.13
100	0	7	0.95±0.01	1.32±0.11
Standard			**> 0.35**	

3. PF can form a thicker interphase than MDI resulting in better adhesion.

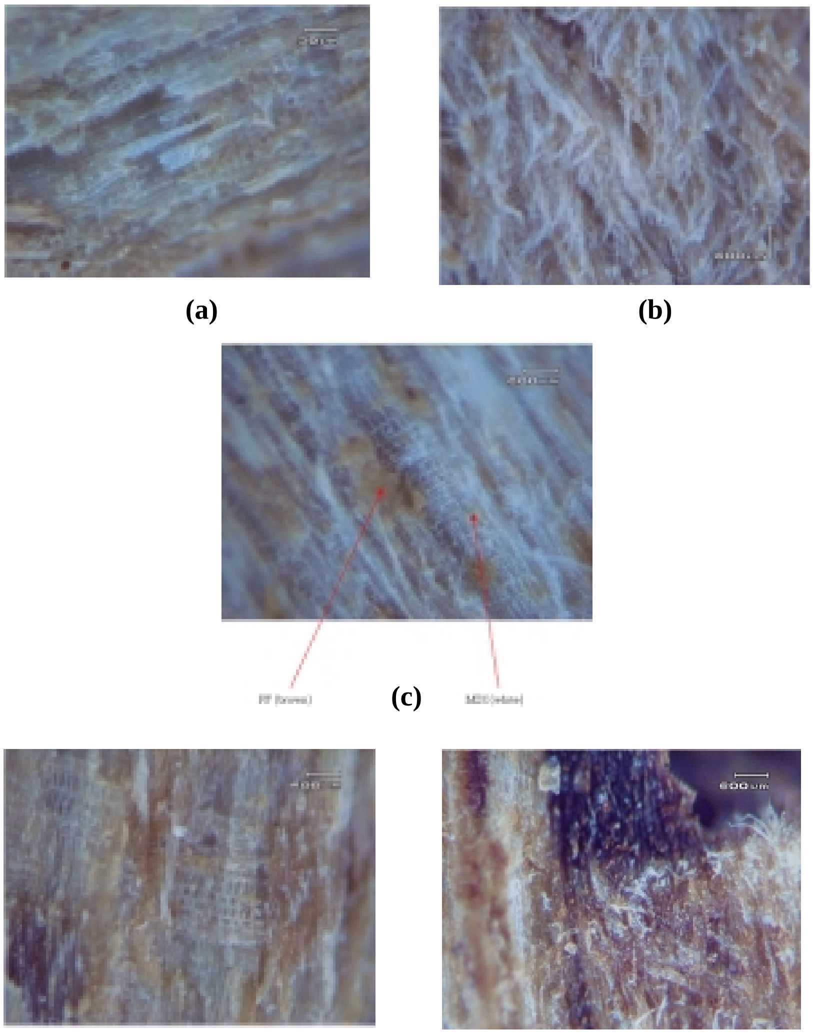
4. The PF molecule can penetrate into the cell wall of wood, so it strengthens the adhesion. However, this phenomenon has not been found in MDI.

Morphology

Surfaces of fractured specimens were investigated using a stereo optical microscope. Fractured surface photographs were taken to see the miscibility of the two adhesives. For sample ratio of 50:50, it is very obvious that the adhesives are immiscible, as one can see two phases very clearly, as shown in Figure 5.

Thickness Swelling

After 24 hour immersion of the OSL in water, thickness swelling of the sample was determined. Results are shown in Table 5.



(a) **(b)**

(c)

(d) **(e)**

Figure 5. Optical micrographs of fractured surfaces of (a) pure MDI (white), (b) 25:75 PF: MDI, (c) 50:50 PF: MDI showing phase separation, (d) 75:25 PF:MDI and (e) pure PF (brown).

(Color figure can be viewed in the electronic version)

Table 5. Thickness swelling (TS) of OSL-adhered by various compositions of PF / MDI blends.

Composition		Thickness Swelling (%)
PF (%)	**MDI (%)**	
0	100	23±6
25	75	13±1
50	50	12±0
75	25	7±1
100	0	5±1
Standard		**< 15**

Table 6. Bond durability or MOR of samples after immersing in boiling water for 2 hours.

Composition		Flatwise		Edgewise	
PF (%)	**MDI (%)**	**BD (MPa)**	**BD/S_g (MPa)**	**BD (MPa)**	**BD/S_g (MPa)**
0	100	3±1	5±0	9±1	14±2
25	75	10±1	14±1	14±5	21±7
50	50	10±4	15±5	16±1	24±1
75	25	14±4	19±4	15±4	23±5
100	0	20±8	25±9	28±2	36±2
Standard		**> 6.2**		**> 14.5**	

The thickness swelling in samples adhered by PF was much lower than MDI (5% compared to 23%). As one increases the percentage of PF in the adhesive, the thickness swelling decreases continuously. This means OSL adhered by PF should last longer under conditions of high humidity.

Standard CSA O437.1-93 allows thickness swelling of 15%. Only pure MDI, that gave 23% swelling, failed to pass the standard. However, if it is necessary to use MDI as the main adhesive, one can mix 25% PF to make the thickness swelling reduce to 13% to pass the standard.

Thickness swelling has two different mechanisms (Wang and Winistorfer, 2003).

1. Swelling of wood: this should not be related to type of the adhesive since it relates to the properties of the wood itself. This type of swelling is "recoverable"

2. Swelling due to relief of residual compression stress is "non-recoverable".

MDI adhesive starts to harden at room temperature while PF starts to harden at a much higher temperature, 160°C (Zheng, 2001). MDI has more residual compression stress since at low temperature, it has high viscosity and does not have enough time for the molecules to relax.

Bond Durability

Bond durability is measured by determining the modulus of rupture of samples immersed in boiling water for 2 hours and then cooled down by immersing in cold water (~20°C) for 1 hour before testing. It was expected that bond durability should show the same trend as "MOR" combined with the "inverse of thickness swelling". Samples with high thickness swelling should have low bond durability. The results of bond durability are shown in Table 6.

Results reveal the same trend as that of the inverse of thickness swelling. Pure PF has the lowest thickness swelling, or the best resistance to water. The result shows the best bond durability of 20 MPa for pure PF while pure MDI has only 3 MPa in the flatwise direction. The results in the edgewise direction show the same tendency. Only pure MDI failed the bond durability test.

Conclusions

From the research work, some conclusions can be drawn:

1. The modulus of rupture and modulus of elasticity in the edgewise direction are larger than those in the flatwise direction due to a larger depth that is subject to load.

2. Phenol-Formaldehyde adhesive gives a much higher internal bonding than MDI due to better adhesion via hydrogen bonding. For adhesive hybrids, the 75:25 PF:MDI hybrid gives the best performance.

3. OSL adhered by PF has a very low thickness swelling while the OSL adhered by MDI has too high thickness swelling and fails to

conform to the standard.

4. Samples with low thickness swelling have high bond durability.

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