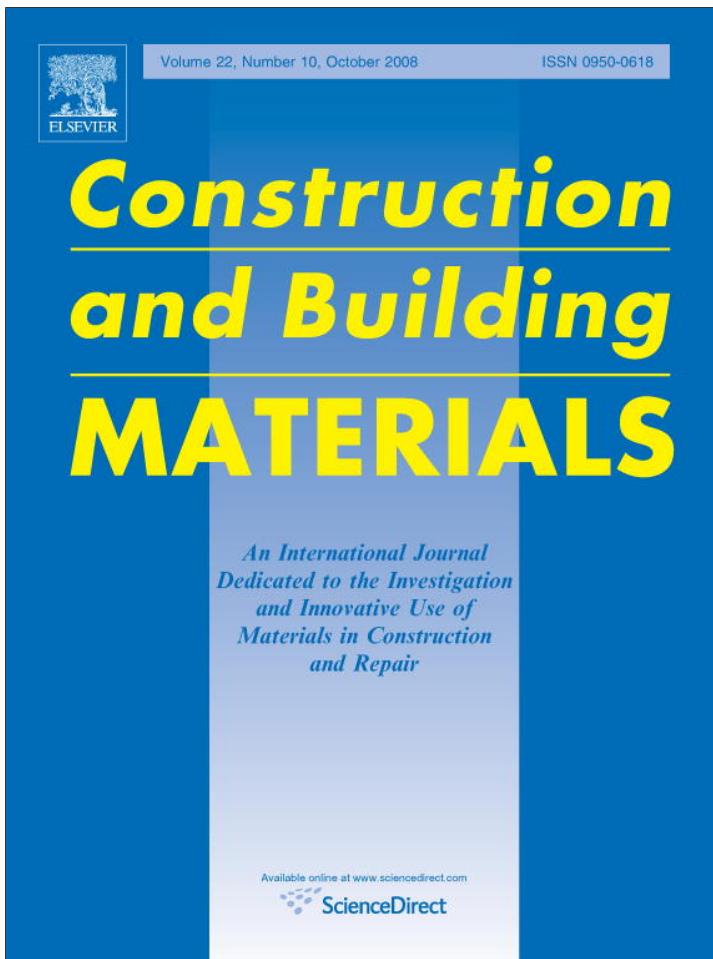


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Fast curing PF resin mixed with various resins and accelerators for building composite materials

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Abstract

The objective of this research is to investigate the fast curing effect of phenol-formaldehyde (PF) resin by employing three methods: mixing with novolac phenol-formaldehyde, adding amino-based resin and the use of accelerators. The effects of shortening phenolic resin curing time and adhesion strength were determined. The gelation time of phenolic resin mixed with novolac resin shortened the curing time by 20–50% compared to that of the phenolic resin itself (at 100 °C). The hot-press time of the phenolic resin was considerably lessened by varying the composition of the amino-based resin, but it introduced the problem of low bonding strength of waterproof layer for plywood constructed with the radiata-pine solid veneer. Among the various phenolic resin types of curing accelerators, sodium carbonate was the most effective and was able to shorten the curing time by 30% when applied to the plywood process. The addition of sodium carbonate as the curing accelerator of a phenolic resin gave a bonding strength of waterproof layer equal to that of phenolic resin (no sodium carbonate addition) and shortened the hot-press time by about 30 s/mm (135 °C). These test results suggested 4–5% as a suitable addition level for sodium carbonate in phenol use.

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Keywords: Fast curing; PF resin; Acceleration; Adhesion; Gelation time; Building composite materials

1. Introduction

Urea-melamine formaldehyde resin (UMF) is mostly used in domestic plywood manufacture. However, the modern performance requirement for highly durable and water-resistant functions has quickly switched the resource supply to the coniferous tree to ensure the fast curing property. Modern environmental considerations have induced the regulation of formaldehyde emissions and the development of energy-saving process. To satisfy these requirements and also gain productivity improvements, it is essential to develop new adhesives while improving the performance of existing adhesives.

Phenol-formaldehyde (PF) resin is mainly used as a binder for waterproof wood panels. Although extensively used, PF resins cure more slowly in a hot wood panel press than aminoplastic resins do [1,2]. The amino-based resin, which is primarily used for interior plywoods such as particleboard (PB) and medium density fiberboard (MDF), is relatively inexpensive and can be manufactured under more moderate conditions than can PF resin. However, it has the disadvantages of causing durability and waterproofing defects and emitting formaldehyde which is harmful to humans. On the other hand, the resol PF resin that is primarily used in the manufacture of structural plywood demonstrates excellent adhesion, but requires higher temperature (135–150 °C) and longer time (45–60 s/mm) than the hot-press condition of amino-based resin [3,4]. Also, most of the structural plywood that is manufactured using the phenol-based resin adhesive is thicker than 28 mm. Any decrease in the hot-press temperature and its

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time reduction (fast curing technology of resin) is highly limited due to the thickness constraint, but is nevertheless very important for energy saving and productivity improvement. In order to reduce the hot-press time of phenolic resin, the following measures have been proposed [5–13]:

- Method 1. polymerization of resin
- Method 2. mixing with novolac PF resin
- Method 3. mixing with amino-based resin
- Method 4. addition of hardener

To achieve fast curing, the following composition variations and phenolic resin manufacture methods have been attempted: process 1 in which the phenol and formaldehyde are reacted in the presence of 2-ply metallic hydroxide, process 2 in which the reaction proceeds in the presence of ammonia or amine compound, and process 3 in which the reaction proceeds in the presence of aliphatic alcohol with a temperature of no more than 90 °C. Tohmura [14] studied the composition of resin and its curing speed in order to accelerate the curing of phenolic resin. They reported that the gelation time increases exponentially according to the increase in the molar ratio of formaldehyde and phenol and that the non-reacted formaldehyde promotes hardening of phenolic resin.

Higichi [15] proved that curing can be effectively accelerated by adding novolac resin. From a study about the manufacture of molecular weight novolac particle with the number-average of 2500, Higichi reported high veneer adhesion with high moisture content and excellent stability of viscosity.

Regarding the melamine resin and phenol/melamine resin, the stability of the plywood quality and the performance can be improved by developing a phenol/melamine resin that allows the hot-press operation at similar conditions to those of the amino-based resin. This is achieved by reduction the hot-press time that is the disadvantage of the phenolic resin and amino-based resin and by substituting phenolic resin and UMF resin that have been used in gluing structural plywood and plywood for concrete molding. More focused and systemized studies have been conducted on the synthesis of phenol/melamine resin, curing mechanism and adhesion performance. As a result, resin curing is largely dependent on the pH of amino-based resin. The curing mechanism under the condition (120 °C, 45 mm) currently being used in the field does not demonstrate better adhesion performance since the phenolic ingredient is not completely cured on the second step after the melamine ingredient is cured on the first step. In order to resolve this problem, longer curing time and the addition of high molecular weight novolac resin have been reported to be effective.

According to research reported thus far, method 1, the polymerization of resin, is effective in shortening curing time, but restricts polymerization due to the worsening work condition with the increasing viscosity. There are a

lot of hardeners could be available to add. However, it will be caused to go up cost. Why I want to reduce hot-press time was to reduce cost. So, only economic methods were considered in this study. Therefore, the present study investigated the fast curing effect and the practical applications of methods 1–3.

2. Experimental

2.1. Resins

Resin was tested in comparison with the laboratory-synthesized phenolic resin. The test phenolic resin (molecular ratio of phenol:formaldehyde:sodium hydroxide = 1:2.0:0.1) and phenolic resin (phenol:formaldehyde:sodium hydroxide = 1:2.2:0.25) were raised to 85 °C in 30–40 min and then synthesized after reaction for 50–60 min. The phenol/melamine resin mixed with melamine resin was made by mixing phenol and melamine with the molecular ratio of 1 after synthesizing phenolic resin (molecular ratio of phenol:formaldehyde:sodium hydroxide = 1:2.5:0.1) and melamine resin (molecular ratio of melamine:formaldehyde = 1:2.5), respectively. The types and characteristics of the resins are presented in Table 1.

2.2. Veneer species

The veneer board used for this test was the currently used DIL (DILENIA) type and the adhesion performance was tested for the plywood produced by mixing the Radiata-pine that is primarily used in the Korean plywood industry.

2.3. Curing accelerator

The novolac resin used for mixing with phenolic resin was from Gangnam Chemical Co., Ltd. in Incheon and the sodium carbonate, formaldehyde and resorcinol used for testing the curing accelerator were all pure chemical reagent grade.

2.4. Gelation Time

The gelation time was taken as the time up to the point that the resin does not flow while agitating the test tube sealed under a water bath and maintaining it at a constant

Table 1
Properties of the test resins

Resins	pH	Viscosity (25 °C, cp)	Solid content (%)
PF-A	8.8	78	46.4
PF-B	9.6	104.5	47.5
PMF	8.6	33	48.7
UMF	7.6	67	53.2

PF-A: phenol:formaldehyde:NaOH = 1:2.0:0.1 (molar ratio).

PF-B: phenol:formaldehyde:NaOH = 1:2.2:0.25 (molar ratio).

PMF: PF(phenol:formaldehyde:NaOH = 1:2.5:0.1) + MF(melamine: formaldehyde = 1:2.5).

temperature after adding 1 ml of resin (mixed with phenolic resin and various additives) in the glass tube with the diameter of 8 mm and length of 10 cm.

2.5. Plywood production and adhesion performance test

Three-ply plywood was produced by using 900 cm² veneer adjusted to ensure a maximum moisture content of 8%. Plywood sample was produced by constructing DIL plywood with DIL(1 mm) + DIL(2.4 mm) + DIL(1.0 mm) and coniferous tree veneer with DIL(1.0 mm) + Radiata-pine(2.4 mm) + DIL(1.0 mm).

The work was conducted for 20 min under the adhesion condition with the spread content of 18 g/900 cm² and cold-press of 10 kg/cm². The temperature, time and resin mixture were also recorded on the respective results. The waterproof adhesion strength of the plywood was measured in comparison with the adhesion strength and wood failure ratio of KS M 3702 after boiling for 24 h.

3. Results and discussion

3.1. Gelation time of phenolic resins

The comparison of resin gelation time, after adding novolac compound and curing accelerator, by using the laboratory-synthesized phenolic resins is shown in the Table 2. A gelation time reduction effect of about 20–50% was observed at 100 °C compared to the laboratory synthetic resin when mixing with novolac phenolic resin. However, the ideal novolac resin for use should be kept with the state distributed on the resol resin until the spreading and gelation of the resol resin is accelerated while resolving them in the cold-press process. The three types of commercially available novolac resins gave relatively good results for gelation acceleration, but suffer the limitation of being clogged into lumps while being resolved into the resol resin. The synthesis of higher molecular weight novolac resin is therefore required.

Sodium carbonate was the most effective curing accelerator of phenolic resin; at 5% addition it reduced the gelation by 65–80% (100 °C) as compared to that of phenolic resin. Therefore, we have reviewed in detail the phenolic resin curing acceleration effect of sodium carbonate.

Table 2
Curing acceleration effect obtained by applying various additives

Additives	Addition level (%)	Viscosity (25 °C, cp)		Solid content (%)
		PF-A	PF-B	
Condition	—	42.8	24.8	
Novlac-A	10	28.4	21.5	
Novlac-B	10	27.6	20.8	
Novlac-C	10	27.6	21.1	
Sodium carbonate	5	8.2	6.8	
Resorcinol	10	22.4	24.4	

3.2. Tendency of sodium carbonate to affect the gelation time of phenolic resin

Fig. 1 shows the gelation time of laboratory-synthesized phenolic resins according to the addition amount of sodium carbonate. The addition of 3% sodium carbonate reduced the phenolic resin gelation time by 63% and 52% at 100 °C. With increasing sodium carbonate addition, the gelation time was reduced; however, the difference was not large. The curing acceleration effect of phenolic resin by sodium carbonate was assumed to be due to carbonic acid ion. If carbonic acid ion simultaneously acts on one hydrogen from one of two methylols and on the oxygen of another methylol, the carbon electron density on one side of methylol is reduced and the oxygen electron density on another side of methylol is increased. Therefore, these carbon and oxygen atoms approach closely and this process illustrates the structure of dimethylene ether. Ultimately, it is converted to methylene bonding and polymerized.

The effect of sodium carbonate on phenolic resin in shortening gelation time and improving adhesion was investigated. Fig. 2 shows the adhesion strength according to sodium carbonate content of plywood manufactured by hot-pressing for 45 s at 135 °C. At 3% sodium carbonate, adhesion strength was doubled. Furthermore, although the adhesion strength and wood failure ratio were increased with increasing sodium carbonate content, there was no significant improvement over 5%. Therefore, the optimum sodium carbonate content was determined to be 3–5% because higher content caused high viscosity.

3.3. Influence of sodium carbonate on the gelation temperature and time of phenolic resin

Fig. 3 compares the hot-press time and adhesion strength of plywood according to sodium carbonate addi-

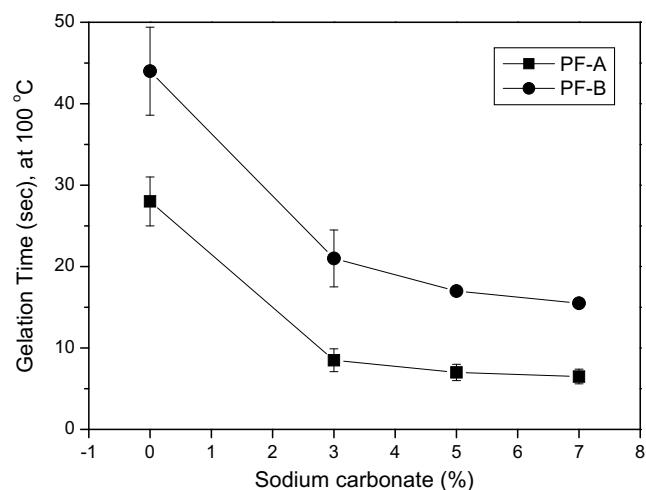


Fig. 1. Gelation time reduction effect according to sodium carbonate addition.

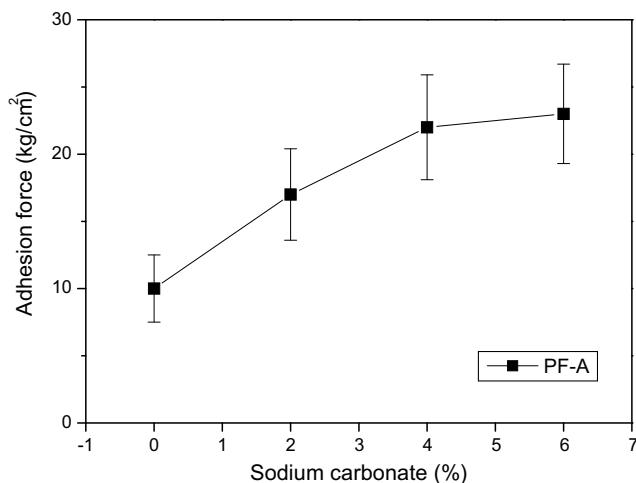


Fig. 2. Correlation between sodium carbonate addition and wood failure ratio of attachment side.

tion. At a hot-press temperature of 135 °C, the adhesion strength was increased with lengthening hot-press time. However, when compared with the similar adhesion performance, 5% sodium carbonate addition exhibited a time reduction of about 30 s/mm as compared to that of no addition. Considering that most structural plywood has a thickness of no less than 12 mm, about half of this hot-press time reduction may contribute greatly to improving productivity. Fig. 4 shows the correlation between gelation time and temperature according to sodium carbonate addition. The effect of sodium carbonate on gelation time reduction was more significant at low hot-press temperature than at high temperature.

These results confirmed the effectiveness of sodium carbonate addition as the curing accelerator for the fast curing of phenolic resin. Therefore, the adhesion performance was compared with that of the phenolic resin mixed with the

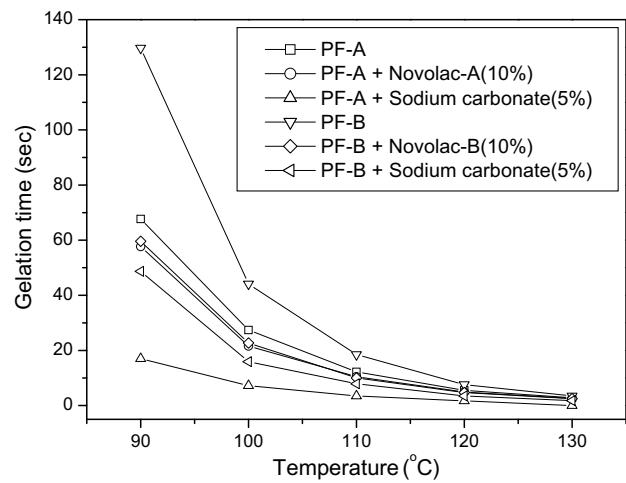


Fig. 4. Correlation between gelation time and temperature.

phenolic resin and amino-based resin that are currently used in the plywood production process.

3.4. Comparison of phenolic resin addition to curing accelerator and the adhesion performance of amino-based phenolic resin

Table 3 shows the result obtained from the addition of curing accelerator to DIL and radiate-pine by using phenolic resins. Tests were conducted for the hot-pressing of phenolic resin at 130 °C for 4 min and of phenol-melamine and urea-melamine resins at 120 °C for 3 min, and the spread content and press condition were 18 kg/cm² and 10 kg/cm², respectively.

The phenol melamine resin with amino-based melamine resin demonstrated the higher adhesion strength than the phenolic resin on the DIL solid, but waterproof adhesion strength decreased. For the urea-melamine resin used in producing plywood of radiata-pine for concrete molding, the adhesion strength was initially satisfactory but subsequently was degraded after 24 h of continuous waterproof performance testing. On the other hand, the addition of sodium carbonate and formaldehyde exhibited excellent waterproof performance in the adhesion strength after 24 h of continuous waterproof adhesion strength testing on the DIL and radiata-pine solid.

The actual process test was performed to check the possibility that the curing acceleration effect obtained from the above laboratory test could be applied in actual factory conditions. After all other conditions were set identically, the reduction of the hot-press time during the property test of the plywood demonstrated the identical waterproof performance suffering the limitation of reduced adhesion strength. In other words, the addition of 4% sodium carbonate reduced the hot-press time by 30% without affecting the waterproof adhesion strength, in comparison to the amount of resin input. Table 4 shows the physical properties of the plywood products produced while applying the hot-press method.

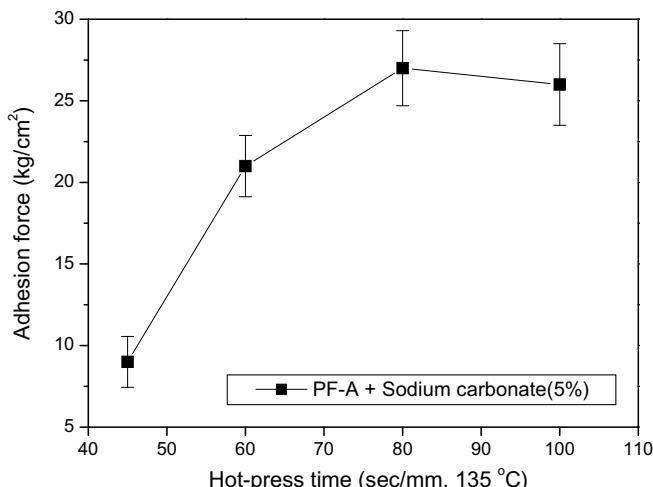


Fig. 3. Comparison of adhesion strength by hot-press time (135 °C).

Table 3
Adhesion strength comparison

Resins	Additive	Adhesion strength (kg/cm ²)			
		DIL + DIL + DIL		DIL + Radiata pine + DIL	
		Dry	24 h boiling	Dry	24 h boiling
PF-B	—	14.6 ± 1.8 (30)	7.5 ± 1.9 (0)	13.2 ± 2.0 (56)	4.8 ± 1.5 (0)
	Sodium carbonate	16.6 ± 1.8 (54)	8.9 ± 1.0 (5)	15.1 ± 2.6 (68)	10.7 ± 1.6 (59)
	Formamide	16.2 ± 1.0 (34)	8.9 ± 0.8 (9)	14.5 ± 2.1 (54)	9.5 ± 2.1 (71)
PMF	—	17.1 ± 1.5 (84)	8.9 ± 1.2 (0)	9.8 ± 1.3 (67)	3.9 ± 1.2 (20)
UMF	—	15.1 ± 11.6 (80)	3.8 ± 1.2 (0)	10.3 ± 1.6 (50)	2

Values within parenthesis: wood failure ratio (%).

Table 4
Result of the hot-press test

Work condition	Dimension		
	9 mm × 4 ft × 8 ft	12 mm × 4 ft × 8 ft	18 mm × 4 ft × 8 ft
(a) <i>Glue type</i>	Phenol + 4% sodium carbonate (curing accelerator)		
Veneer moisture ratio (%)	7–9	7–9	7–9
Hot-press temperature (°C)	135	135	135
Hot-press time	9 min → 6 min	12 min → 8 min	16 min → 12 min
(b) <i>Waterproof adhesion strength (kg/cm²)</i>			
Waterproof adhesion strength	14.0	14.3	11.7
Boiling for 24 h	12.8	11.8	9.5

4. Conclusion

This study investigated the reduction of hot-press time in the use of novolac phenol resin for producing plywood from phenolic resin. The acceleration effect on curing time by adding an amino-based resin to the phenolic resin was also examined, along with the adhesion strength. The following conclusions were obtained.

1. The gelation time of the phenolic resin mixed with novolac resin exhibited a shortened curing time of 20–50% compared to the pure phenolic resin (at 100 °C). However, the novolac resin suffered a clogging problem when mixed with the resol type of phenolic resin and further improvements are necessary from the technical perspective.
2. The composition of the amino-based resin could considerably lessen the hot-press time of the phenolic resin, but it introduced the problem of lowering the bonding strength of waterproof layer for the plywood constructed with the radiata-pine solid veneer.
3. Among various types of phenolic resin acting as curing accelerators, sodium carbonate was the most effective and shortened the curing time by 30% when applied to the plywood process.
4. The addition of sodium carbonate to a phenolic resin as the curing accelerator achieved a bonding strength of waterproof layer equal to that of phenolic resin (no sodium carbonate addition) and shortened the hot-press time by about 30 s/mm (135 °C). According to the test results, the most effective sodium carbonate content was about 4–5% of the phenol amount.

Compared to existing urea/melamine resin, the application of phenolic resin to plywood afforded superior quality in terms of physical properties. The productivity limitations and work difficulties arising from the use of phenolic resin may be compensated by using sodium carbonate as a curing accelerator.

Acknowledgement

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