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Dry-heat Degradation of Plywood-type Joint*

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Abstract—In order to predict the service life of plywood heating floors, dry-heat exposure test of lauan plywood made with each of six type of typical wood adhesives was carried out at 50°, 70°, 100° and 150°C for 250 days. Internal bond strength and location of failure of the exposed specimens were measured at selected intervals. Data were plotted as a function of the exposed time. Confidence limit was applied on the regression and the service life was calculated by extrapolating the lower confidence limit curve to the half-strength. The apparent mechanism of dry-heat degradation of plywood in 150° and 100°C seemed to differ from the lower temperature exposures. On 70° and 50°C, more conservative estimation was made by the kinetic method on the Arrhenius relationship. The result showed the detrimental effect of the acid catalyst on polyvinyl-acetate cross-linked and urea resin adhesives. Plywood specimens produced with melamine, phenol, phenol-resorcinol, and resorcinol resin adhesives showed excellent durability in dry-heat exposure at temperature normally found in service of floor heating.

Introduction

Heating floor of house buildings is expected as one of the most effective and comfortable room-warmers, as it brings an uniformly distributed temperature in living space and economy in heating energy due to effective use of the radiant heat from the surface of the floor.

A distinctly high value of the radiant efficiency of wood¹⁾ and the good texture and tactile impression of wood²⁾ with the living comfort of biological materials are prominent indications to the usefulness of wood as heating floor materials.

This research was planned as a part of the comprehensive research on performance of heating-floor of wood-based materials. The major objective of this research is to predict the service life of plywood type floorings subjected to the floor heating.

By now, most studies concerning degrading of plywood type bond due to heat (Gillespie^{3,4,5)}, Gamo⁶⁾, Horioka⁷⁾ and Northcott⁸⁾) have been done on temperatures higher than those normally found in service of floor heating and in most cases involving moisture. The extent of deterioration has been determined by measuring plywood tension shear strength as a function of exposure time to specific

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temperatures. Determination of service life by extrapolating those data to a temperature of floor heating (about 50°C) may not be expected as the half-life obtained by the tension shear strength of plywood specimens is not precise enough to the purpose because of the high stress concentration in the specimen. Use of more reasonable type of specimen and statistical treatment of the data are needed.

In this study, dry-heat exposure tests were done on lauan plywoods made with each of six different adhesives for 250 days at temperatures including that of normally used in floor heating. Internal bond strength test method (Tension perpendicular to surface) was adopted in this experiment. Stress concentration in the specimen is not so high (rather even) as that in plywood tension shear specimen and the location of failure indicates the weakest layer of a specimen at specific exposure time and these are good advantage for discussion of the apparent mechanism of degradation. In addition to this, a concept of confidence limit curve of the regression was introduced to predict the service life in the safer way than the past.

It would be interesting to compare the results to the kinetic studies^{9~12)} of the degradation of wood-glue system and to the study on low-temperature degradation¹³⁾ of wood-glue bond.

Experimental Procedure

Materials

Six commercial wood adhesives were used. The mixing instructions recommended by the manufacturers were followed and curing temperature and press time were

Table 1. Composition, formulation and curing conditions of Adhesive resins used in this study.

Resin	Composition	Formulation (phr)	Curing conditions
Polyvinyl-acetate cross-linked (PVA-C)	PVA-C resin 60 % Phenol resin 40 %	resin 100 hardner (sulfonic-acid type) 10	130°C for 4 min
Urea-formaldehyde (UF)	molar ratio is 1U : 1.9F	resin 100 wheat flour 10 water 15 hardner (NH ₄ Cl) 1	130°C for 4 min
Melamine-urea formaldehyde (MUF)	melamine 24 % urea 6 % 37 % formalin 70 %	resin 100 wheat flour 13 water 7 hardner (NH ₄ Cl) 1	130°C for 4 min
Phenol-formaldehyde (PF)	molar ratio is 1P : 2F	resin 100 extender 5	145°C for 4 min
Phenol-resorcinol formaldehyde (PRF)	phenol r. 15 % resorcinol r. 85 % molar ratio is 1 : 0.8F	resin 100 hardner (paraform) 20	130°C for 4 min
Resorcinol-formaldehyde (RF)	resorcinol resin 100 %	resin 100 hardner (paraform) 15	130°C for 4 min

partly increased to insure complete cure had taken place. These conditions are described in Table 1. All resin spreads were controlled in 30 g/ft² of double glue-line.

For each adhesive, four three-ply plywoods were made of air-dried lauan rotary veneers of dimensions 45 by 45 cm. The thickness constructions of veneers of the plywoods were 2 mm each for the face and back and 3 mm in the core. Total open and closed assembly time was kept to less than 25 minutes. The plywoods were made at a pressure of 5 kg/cm².

Sixty-four strips of 5 by 5 cm were cut from each panel giving 256 strips for each adhesive and 178 strips of which were randomly selected to this experiment. Eighteen strips for each resin were retained for control purpose and the remaining 160 strips were randomly placed in four groups of 40 each for four conditions of temperature of exposure.

Dry-heat Exposure

Four automatically temperature-controlled ovens were used and during this study, it was estimated that the change of temperature was not greater than $\pm 1^\circ\text{C}$ of the average. Temperatures of these ovens were controlled to 150°, 100°, 70° and 50°C respectively.

Fifty degree C is normally found in subflooring of the floor-heating in service. Increased temperatures were used to determine degradation due mainly to thermal deterioration in the absence of moisture, because very low moisture content of the heating subfloor was found and the influence of moisture on the degradation was thought to be neglected.

Hundred-twenty strip specimens which consisted of 20 specimens of each type of adhesives were randomly put on to four shelves in each oven. Positions of the shelves were changed with each other at suitable intervals so as to reject the influences of different locations within the oven space.

Strength Test

Data were determined as a function of exposure time in each environment. Groups of six specimens of different kind of adhesives were removed from each oven at selected intervals for internal bond strength measurement and estimation of location of failure occurred. All specimens were tested immediately after removal from the ovens, and actually moisture contents of the specimen at test were not greater than 2%.

All measurements for internal-bond strength were made according to the procedures described in ASTM-D-1037-72a¹⁴⁾ (Tensile strength perpendicular to surface — see Fig. 1). In order to compare these data with the strength before

exposure, 18 specimens per each type of adhesive were dried in a desiccator at room temperature to about two percent of moisture content and internal-bond strengths were measured by the same method as mentioned above.

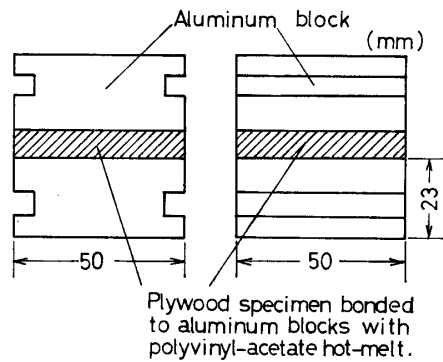


Fig. 1. Specimen and attachment blocks for testing internal-bond strength.

Analysis of Data

Internal-bond strengths were plotted against the exposure time, and the least squares regression curves (or lines) were calculated to each temperature and adhesive.

First and second degree polynomials of the following general form were applied to the regression:

$$Y = \sum_{i=1}^n A_i X^i$$

Expression (1) to (8) listed in Table 3 were used as the fitting curves, where σ is observed strength at exposure time t , σ_0 is the average strength of the control specimens, A is a constant and t is exposure time.

The deviations of the data from the regression curves were compared and the most suitable expressions of these eight forms for each condition of temperature and adhesive were determined.

In order to be able to predict the service life of heating subfloor in a safer measure, a concept of the lower confidence limit of the regression curves was introduced. The procedure is as follows:

The variance of observed data from the regression curve S^2 is

$$S^2 = \frac{\sum_{i=1}^n \{\sigma_i - f(t)\}^2}{N - M - 1}$$

where σ_i is observed strength of the i -th specimen of which exposure time is t , $f(t)$ is the value of the regression curve for exposure time t , N is the total number of specimens tested and M is the degree of the regression polynomial, and $N - M - 1$ means the degree of freedom.

Then, the lower confidence limit of the regression curve $f_c(t)$ can be expressed as

$$f_c(t) = f(t) - U(\alpha)S,$$

where, $U(\alpha)$ is the width taken around the average in the standardized Gaussian distribution corresponding to the given confidence coefficient α . For instance, when α is 0.95, $U(\alpha)=1.96$ and when α is 0.99, $U(\alpha)=2.57$.

Introducing this concept, the lower confidence limit is also a function of exposure time t , and the service life which is taken conventionally as an exposure time required to degrade to the half strength at the specific temperature can be determined with desired confidence coefficient on extrapolating the lower confidence limit curve to the half strength.

Results

Control Test

Results of tests on the control specimens are summarized in Table 2. Strengths for specimens bonded with adhesives except PVA-C were substantially of the same values. Those strengths of 12~14 kg/cm² coincide with the general level of high quality bonded lauan plywoods. PVA-C resin required sulfonic acid type catalyst to cure and though it was naturally used as room-temperature cure adhesive, hot-pressing was adopted to insure complete cure before dry-heat exposure. Most locations of failure in PVA-C bonded specimens were in the wood directly adjacent to the bonding interface (Fig. 3 a). The lower strength value (7.7 kg/cm²) for PVA-C bonded specimens was therefore interpreted as being caused by the detrimental effect of the acid catalyst that was accelerated by hot pressing at 130°C.

Table 2. Initial internal bond strength of plywoods used in this experiment.

Adhesives used	Strength* σ_0 (kg/cm ²)	Half strength $\sigma_0/2$ (kg/cm ²)	Standard deviation S_0 (kg/cm ²)
Polyvinyl-acetate cross-linked (PVA-C)	7.7	3.9	1.76
Urea-formaldehyde (UF)	13.7	6.9	1.55
Melamine-urea formaldehyde (MUF)	12.6	6.3	1.38
Phenol-formaldehyde (PF)	12.4	6.2	1.23
Phenol-resorcinol-formaldehyde (PRF)	13.8	6.9	1.88
Resorcinol-formaldehyde (RF)	13.5	6.8	1.31

* Average of 18 specimens dried in a desiccator 1~2% of moisture content.

The wood failure values for the specimens bonded with PF and MUF were lower than those with other adhesives, and this appeared to be due to the incomplete cure of the resins (Fig. 3 c,d).

Strength Degradation

The regression curves of the first and second degree polynomials (expression (1) —(8) in Table 3) were calculated on strength-exposure time data with use of the control test values as data at exposure time of 10 sec. Averages of sums of square of deviation from each regression curve for adhesives were calculated and shown in Table 3. In the table, the best fitting regression was found on the expression (4) for all exposure temperature and the second best appeared to be the expression(7).

The expression (2) which was used by Northcott et al.^{7,8)} appeared the third best fitting but the better fittings were not expected on the expression (8)^{3~6)} and others.

Table 3. Average of sum of square on error from the regression curve.

Regression curves	$Y = \sum_{i=0}^n A_i X^i$		n=1				n=2			
	Y	X	50°C	70°C	100°C	150°C	50°C	70°C	100°C	150°C
1	σ/σ_0	t	10314	10890	12740	34801	9185	9689	10217	18172
2	σ/σ_0	\sqrt{t}	9046	9326	9660	16242	8310	8328	7689	7272
3	σ/σ_0	1/t	8645	8492	9172	29722	8554	8134	8365	19358
4	σ/σ_0	log t	8309	8119	7912	10564	8203	8081	7204	5602
5	$(\sigma/\sigma_0)^2$	t	10754	11620	8877	>99999	9482	10034	11230	>99999
6	σ/σ_0	t	10471	11015	13146	79252	9284	9748	10264	48515
7	log(σ/σ_0)	log t	8420	8230	8039	61392	8262	8140	7311	13907
8	log(σ/σ_0)	t	10229	10763	12440	26628	9091	9569	9902	10150

====: the minimum, —; : the minimum but one, : the minimum but two.

Following this result, internal bond strength data (σ/σ_0) were plotted against log exposure time (log t) as shown in Fig. 2a~2f.

In spite of the low initial strength, PVA-C bonded plywood lost strength more rapidly than the others, as the degradation of strength in PVA-C plywood was mainly due to chemical reaction of acid catalyst. In fact, the failed surface was carbonized dark in color.

Acid catalyst was also used to cure UF bonded plywood, and the degradation of strength had the same but much less tendency as that of PVA-C bonded specimens. These detrimental effect of the acid catalyst has been pointed out by Gillespie⁴⁾.

On the other hand, at low temperature as 70° and 50°C strength of PF bonded specimens had a slight tendency of increasing with exposure time, which appeared to be related to the post-curing of the resin. The same effect might be expected on MUF bonded specimens, as the wood failure was not dominant in the control specimens (see Fig. 3c).

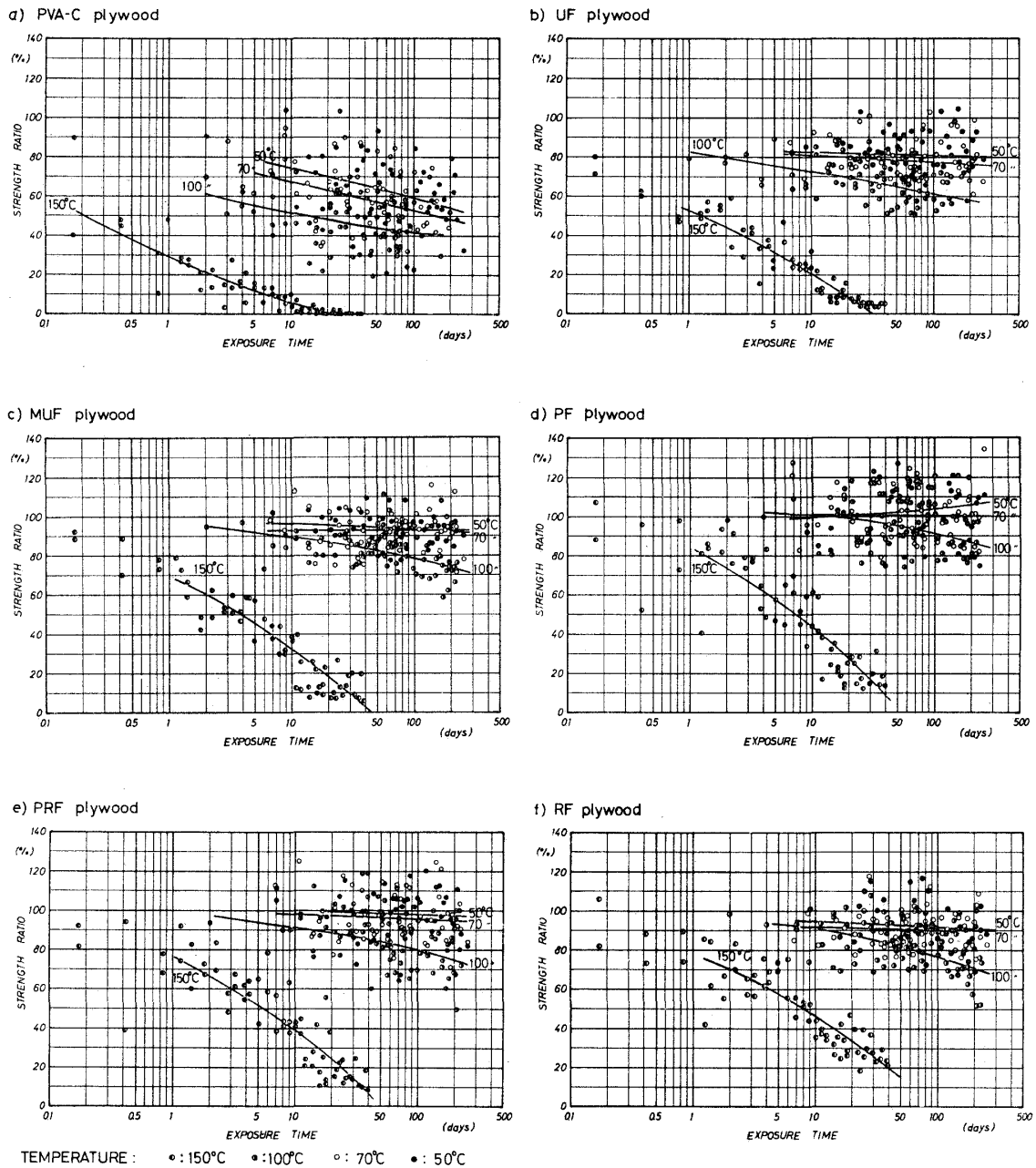


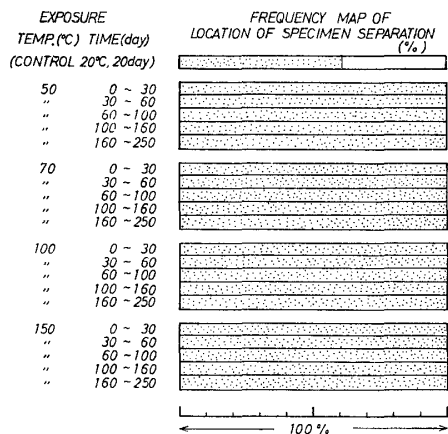
Fig. 2. Internal bond strength as a function of exposure time at different temperature.

Figures for PRF or RF bonded specimens appeared a little to differ from that of PF bonded. It was typically shown on the curves for 100° and 150°C that the formers had gently sloping form while the latter decreased slowly at first, then rapidly.

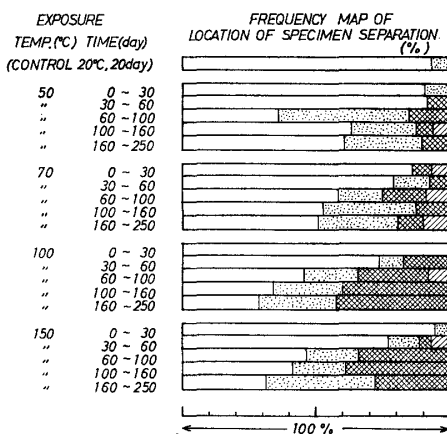
These were interpreted as being caused by the post-curing effect of PF glue. From this, it is thought that but for the post-curing effect, the degradation of PF bonded specimen might be about the same as that of PRF or RF bonded specimens.

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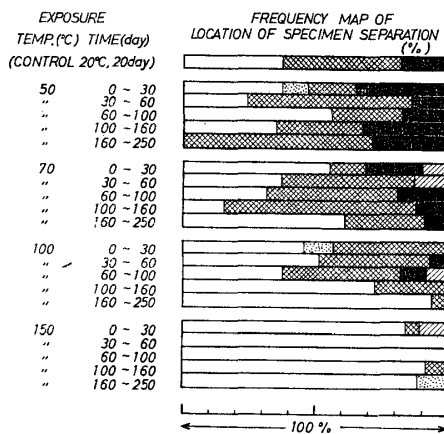
a) PVA-C plywood



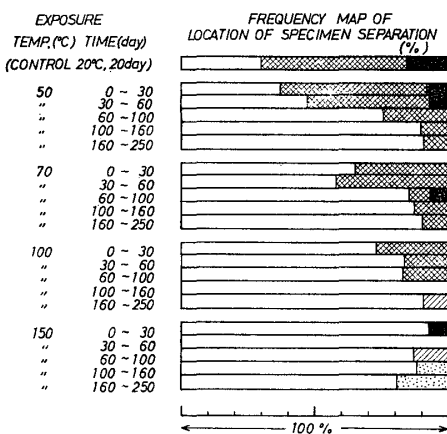
b) UF plywood



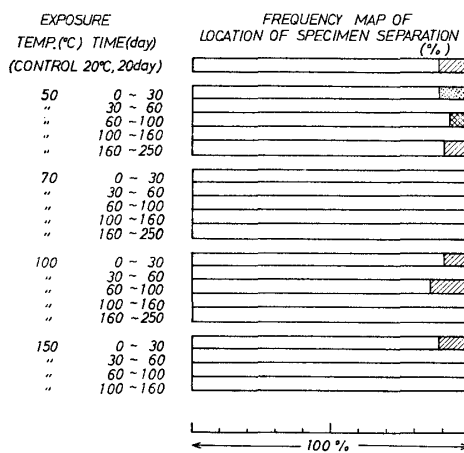
c) MUF plywood



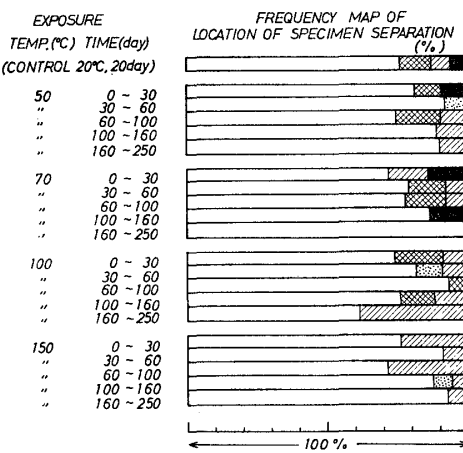
d) PF plywood



e) PRF plywood



f) RF plywood



: in face or core veneer
 : in glue-line
 : mix of wood and glue-line
 : in wood directly adjacent to glue-line
 : in core veneer

Fig. 3. Frequency map of location of specimen separation in percent within different ranges of exposure time.

Location of Specimen Failure

The locations of failure in all specimens were classified into following five cases:

- 1) Separation in the face or back veneer,
- 2) Separation in glue-line including the bonding interface,
- 3) Separation partly in glue-line and partly in wood,
- 4) Separation in wood directly adjacent to the bonding interface,
- 5) Separation in the core veneer.

Whole exposure time 250 days was partitioned into 4 or 5 ranges of exposure time, and in every range the frequencies of the five cases of specimen separation mentioned above were calculated in percent. Figs. 3a~3f summarize the results as histograms.

All separations of exposed PVA-C specimens occurred in wood directly adjacent to the bonding interface, and this indicates the chemical degradation of wood with acid catalyst. The same detrimental effect of catalyst could be seen in that the frequency of this type of separation in UF bonded specimens increased with increasing exposure time.

Frequency of glue-line failure in MUF and PF bonded specimens decreased with increasing both temperature and time of exposure. This fact indicates clearly the post-curing of these resins.

PRF and RF bonded specimens showed fairly consistent figure of separation, and this means the perfect cure at hot-pressing.

Discussions

Half-strength values of specimens bonded with different adhesives are shown in Table 2. The half-lives were calculated by extrapolating the lower confidence limit curves to the half-strength. The confidence coefficients 0.95 and 0.99 were used in the calculations. The meanings of these numbers 0.95 and 0.99 are that the estimations include errors less than 5% and 1% respectively.

Table 4 summarizes the calculated results. Most of the half-lives calculated for low temperatures as 70° and 50°C were too big number to estimate, because the curves were nearly parallel to the time axis and the estimation of the half-lives could not be expected to be exact. These are expressed as $>10^8$ in the table.

These half-lives appear somewhat eccentric for low temperature degradation, for instance incredibly high resistance of UF bonded specimens at 70°C etc... The correction of these results might be needed, as there is no reliable theory to predict the half-life on extrapolating the data in which the degradation is not clear enough.

Auxiliary trial was made to extension of the kinetic method of approach. Log

Table 4. Half life calculated by quadratic function of log *t* fitted on data within 250 days exposure. (unit: days)

Adhesives used	Confidence coeff.=0.95				Confidence coeff.=0.99			
	Exposure temperature (°C)				Exposure temperature (°C)			
	150	100	70	50	150	100	70	50
Polyvinyl-acetate cross-linked (PVA-C)	8.42 × 10 ⁻²	2.40 × 10 ⁻¹	2.12	7.33	6.63 × 10 ⁻²	9.02 × 10 ⁻²	4.15 × 10 ⁻¹	1.45
Urea-formaldehyde (UF)	5.46 × 10 ⁻¹	4.40 × 10	>10 ³	>10 ³	4.07 × 10 ⁻¹	1.53 × 10	>10 ³	>10 ³
Melamine-urea-formaldehyde (MUF)	1.25	8.63 × 10 ²	>10 ³	2.64 × 10 ⁶	8.49 × 10 ⁻¹	5.17 × 10 ²	>10 ³	8.27 × 10 ⁵
Phenol-formaldehyde (PF)	2.16	1.75 × 10 ³	>10 ³	>10 ³	1.36	8.26 × 10 ²	>10 ³	>10 ³
Phenol-resorcinol-formaldehyde (PRF)	1.62	2.58 × 10 ²	6.95 × 10 ⁶	5.98 × 10 ⁶	1.03	9.46 × 10	7.74 × 10 ⁵	8.57 × 10 ⁵
Resorcinol-formaldehyde (RF)	2.41	3.57 × 10 ²	>10 ³	1.62 × 10 ⁷	1.59	1.49 × 10 ²	>10 ³	1.04 × 10 ⁶

reciprocal half-lives calculated above were plotted as a function of reciprocal absolute temperature of the exposure, and these are shown in Fig. 4 for confidence coefficient 0.95 and in Fig. 5 for 0.99.

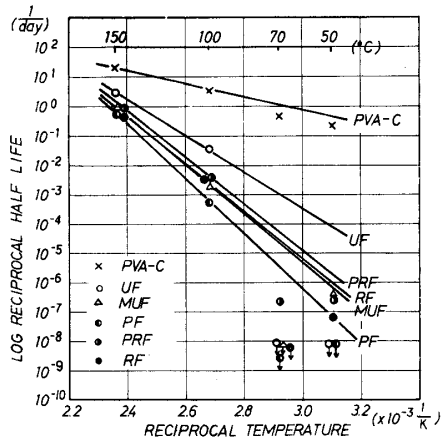


Fig. 4. Log reciprocal half life as a function of reciprocal absolute temperature (Half life at confidence coefficient 0.95).

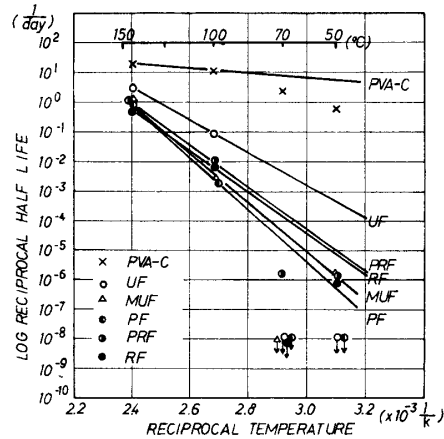


Fig. 5. Log reciprocal half life as a function of reciprocal absolute temperature (Half life at confidence coefficient 0.99).

If, as references^{3,4,15)} have suggested, for all these temperatures the deterioration of strength results mainly from chemical changes in the substance being aged, and if the effect of post-curing is over for the present data of 150° and 100°C exposure, the reasonable half-life might be found in extrapolating the 150° and 100°C data to the lower temperatures.

The extrapolation with straight lines showed that the half-lives obtained by

this procedure are much conservative values than those from extrapolations of the lower confidence limit curves.

As the purpose of this study is to predict the reliable service-lives of plywood floor, the more conservative value would be appreciated. Recommendable service lives determined as round numbers of the reciprocals of values of the lines at specific temperatures in Figs. 4 and 5 are shown in Table 5.

Table 5. Recommendable service-lives of plywoods in dry-heat conditions.

Adhesive resins used	Temperature exposed				
	150°C	125°C	100°C	75°C	50°C
Polyvinyl-acetate cross-linked (PVA-C)	1~ 2 h	1.5~ 3 h	2~ 5 h	2~ 11 h	4.5~ 20 h
Urea formaldehyde (UF)	9~ 13 h	1.5~ 4 d	15~ 40 d	140~400 d	5.5~ 25 y
Melamine-urea formaldehyde (MUF)	20~ 30 h	8~ 20 d	1~2.5 y	25~ 80 y	2500~ 6500 y
Phenol formaldehyde (PF)	1~ 2 d	10~ 45 d	2~4.5 y	40~250 y	5500~40000 y
Phenol-resorcinol formaldehyde (PRF)	1~1.5 d	5~ 10 d	90~250 d	13~ 25 y	270~ 1000 y
Resorcinol formaldehyde (RF)	1.5~ 2 d	10~ 13 d	140~350 d	9~ 25 y	380~ 1000 y

h : hours, d : days, y : years

The minimum value of service-life range was estimated on confidence limit 99% and the maximum on 95%.

The longest service life can be supplied by PF bonded plywood floors and the absence of moisture allows MUF bonded floors to have the second best resistance. As both PRF and RF bonded floors have no post-curing effect of adhesives like PF and MUF, their service-lives at low temperatures are unexpectedly short. Any way, in conclusion, plywood floors bonded with these four adhesives have good enough durability when they are used as floor or basefloor in usual floor heating condition.

For reference purpose, the activation energies were calculated from the slopes k of the lines in the Arrhenius relations of Figs. 4 and 5 using the well-known equation as,

$$\log k = \frac{-E_A}{2.303R} \frac{1}{T} + \text{const}$$

where E_A is the activation energy, R is the gas constant, and T is the reciprocal absolute temperature of the exposure.

The calculated results are as follows:

- for PVA-C: $E_A = 3.9 \sim 10.1$ Kcal/mol
- UF : $E_A = 24.6 \sim 28.5$ Kcal/mol
- MUF : $E_A = 36.9 \sim 38.5$ Kcal/mol
- PF : $E_A = 43.5 \sim 46.5$ Kcal/mol
- PRF : $E_A = 32.3 \sim 36.9$ Kcal/mol
- RF : $E_A = 31.5 \sim 36.9$ Kcal/mol

These values are larger to some extent than those reported on thermal degradation of wood-adhesive system in the presence of moisture^{4,5)} and of wood and cellulose¹⁵⁾.

Acknowledgments

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