Hygroscopicity of Archaeological Timber: Effects of Molecular Weight of Impregnant and Degree of Degradation

I. D. MacLeod

Western Australian Maritime Museum
Cliff Street.
Fremantle, Western Australia, 6160

The weights of the treated wood samples were determined in May 1988 after nine months of storage in the *Batavia* gallery (22°C and 55% RH) and again immediately before packing in February 1989 after eighteen months storage, but when the relative humidity was approximately 60%. It was noted that the acetone-rosin treated samples all lost a substantial amount of solvent during the nine-month period between weighings with an average weight loss of 27.5% compared with a mean loss of 0.41% for the air-dried reference samples. The most stable samples were those from the radiation cured polymer treatment in Grenoble with a mean increase in weight of only 0.02%. The Sawada treated samples appear to be giving off sane solvent, but to a much smaller extent than the acetone-rosin treated material. The results of all the different methods on the seven wood samples are summarised in Table I where we see that even after two years, the air-dried PEG 4000 treated wood is still giving off moisture, but to a lesser extent than the air-dried reference materials. The use of lower molecular weights of PEG in conjunction with air-drying tends to make the treated wood more hygroscopic. When a low molecular weight PEG is followed by a higher weight in a different solution the inherent hygroscopicity of the PEG 200/400 appears to be masked. The use of diethylene glycol on the jarrah sample resulted in a weight increase of 17.2% and great care would need to be taken to avoid problems associated with hygroscopic surfaces if the use of this impregnant was adopted.

Table I: Weight Changes in Storage of International Timber Samples

	Mean Change	Standard Deviation	
	wt%	wt%	Comment
Acetone-rosin air	-27.5	21.0	Strong acetone smell
W.A.M.M. PEG 1500	-1.5	1.84	Insufficient drying
Nara PEG 4000 t-Butanol	-1.12	1.3	Possible loss of t-butanol
Air-dried reference	-0.41	0.34	
Trondheim PEG 4000 air	-0.29	0.11	Slow air-drying
Netherlands PEG 4000 i-PrOH/tBUOH	-0.21	0.74	-1. 72 for worm eaten jarrah.
Grenoble radiation resin	+0.02	0.17	
Hoffmann PEG 200 and 3000 air	+0.08	0.09	
Austria PEG 400	0.14	0.25	No difference in ARCS 1 and 2
English Heritage PEG 400 + 4000	0.17	0.14	
Hoffmann PEG 200 air	0.39	0.04	
CCI PEG 400 + 3350	0.62	0.37	Max. increase for SWTG
CCI PEG 1450	0.63	0.23	
Grenoble PEG 400 + 4000	0.73	0.45	Max. increase for SWTG
Trondheim PEG 400 air	0.99	0.37	Max. increase for SWTG
Hoffmann diethylene glycol	17.2	-	Used only for jarrah

Whilst there were insufficient samples of timber treated by radiation polymerization and acetone-rosin to properly compare the programmes with each other, there were a large number of PEG treated samples. From the individual timber specimens treated in the different laboratories we were able to draw up the data listed in Table II, which summarises the weight changes as a function of the molecular weight of PEG. As previously noted, the data from twinned PEG treatments used by the Canadian Conservation Institute, Per Hoffmann and the English Heritage group are not included owing to the masking effect of the higher MW grades on the hygroscopicity of PEG 400 or PEG 200. One of the reasons for the large standard deviation of the mean weight percent changes is due to variables such as percent of PEG impregnant in the treatment solutions and the entrapment of solvent/PEG in wormholes. Inspection of the data in Table II shows that the percent change in weight during storage appears to be clearly dependent on the MW of the PEG.

The effect of the degree of degradation of the timber samples is a little difficult to determine directly from the data as presented in Table II. However, when the mean weight percent changes are plotted as a function of PEG molecular weight they conform to linear equations of the type,

$$\Delta w = H - k\,(MW)$$

where Δw is the change (wt%), MW the molecular weight of the PEG, k is a constant and H is the intercept at zero molecular weight and a measure of the inherent hygroscopicity. The correlation coefficients for the least squares fit range from 0.97 to 0.99, which is remarkably good for archaeological material treated in different laboratories around the world! The values of H and k are listed in Table III along with the mean values of U_{max}, the maximum weight percent water present in the samples before treatment. It should be noted that values of U_{max} can vary significantly depending on the heterogeneity of the sample. For wood samples of the same species it is very clear that higher H values are associated with higher values of U_{max}. This is probably a reflection of the fact that more PEG has been incorporated into the more extensively degraded timber and as such the treated sample will be inherently more hygroscopic. The rate at which the woods' hygroscopicity decreases with increasing molecular weight (k) is also dependent on the degree of degradation since, in general, a higher U_{max} results in a higher value of the constant k. For the two spruce samples from Canada and Norway the slightly greater intercept of the Norwegian sample and its greater H and k values mirror the differences in the extent of degradation as reflected in the higher U_{max} value.

Although the number of samples of the heavily degraded oak from Somerset Levels was limited to only two it had the greatest H value compared with the Day Dawn (minimal degradation) oak and that of the moderately degraded oak from the Netherlands which all follow the trend of the Umax values. Not too much credence should be placed on the individual values of the constants H and k for the Somerset Levels, since there are no other wood samples of the same species from different sites, with which to make comparison. The data for the alnus samples are apparently anomalous since the high H values for the populus sp. and the corylus sp. agree with the high value for the oak wood. In summary we can definitely conclude that the more extensively degraded the timber the greater will be its inherent hygroscopicity owing to the greater uptake of polyethylene glycol. Since the equations describing the rate at which hygroscopicity changes as a function of molecular weight are linear it is very easy to calculate a theoretical value of the PEG MW that will give no response to changes in RH. For the minimally degraded Jarrah the MW would need to be greater than or equal to 1000 whilst the Somerset Levels oak would require a MV of the order 4300. The other calculated values are listed in Table III. There is a need *for* compilation of more data on the way in which PEG treated archaeological timber changes with relative humidity, but the information obtained from the Comparative International Wood Study programme has' pointed the way. Conservators now have a proper basis on which to make their choice of treatments.

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Table II: Weight changes during storage of PEG treated timbers

	Molecular weight of PEG used			
	4000	3000	1500/1450	400
Origin and type	wt% SD	wt%	wt% SD	wt% SD
Norway spruce	-0.35 ± 0.52	-	0.44	0.6l ± 0.31
Canadian spruce	-0.23 ± 0.35	-	0.43 ± 0.81	0.58 ± 0.76
Jarrah	-1.8l ± 1.61	-	-0.12 ± 0.84	0.24 ± 0.31
Day Dawn oak	-0.06 ± 0.28	-	0.37 ± 0.75	0.67 ± 0.86
De Jong oak	-0.82 ± 1.28	-0.05	0.37 ± 1.14	0.76 ± 0.29
Somerset Levels oak	+0.08	-	0.83	
Sawada chestnut	-0.14 ± 0.26	-0.07	0.15 ± 0.95	0.53 ± 0.62
Somerset Levels populus	-0.12	-	-	1. 74
Somerset Levels alnus	-	0.16	0.56	-
Somerset Levels corylus	+0.08	-	-	1. 30

Table III:
Hygroscopicity Parameters for PEG Treated Wood

Type	Origin	intercept (H)	slope x IO^4	Umax % mean	Calc. MW zero change
Spruce	Canadian	0.71	-2.3	186	3086
Spruce	Norwegian	0.77	-2.8	225	2750
Oak	*Day Dawn*	0.71	-1.9	221	3620
Oak	De Jong	0.98	-4.5	304	2177
Oak	Somerset Levels	1.28	-3.0	1000	4266
Jarrah	Long Jetty	0.59	-5.9	149	1000
Alnus sp.	Somerset Levels	0.16	-2.8	930	571
Populus sp.	Somerset Levels	1.95	-5.2	1323	3750
Corylus sp.	Somerset Levels	1.44	-3.3	-	4363
Chestnut	Japan	0.61	-1.8	403	3388