Color Change in Thermally-modified Wood and its Relationship with Property Changes

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INTRODUCTION

In the woodworking industry image analysis is routinely used for quality control and for matching and classification during various processes. An extension of these automated systems for the prediction of physical properties of thermally-modified wood (TMW) is enticing, because to date there is no a generalized procedure for the quality assurance of this material. The purpose of this work was to investigate the relationship between property changes in TMW and heated-induced colour changes. A description of the effect of the temperature and time of treatment on colour variables and its relationship between these and colour changes in Klason lignin is also given.

EXPERIMENTAL

Small, matched specimens ($150_l \times 20_r \times 10_t$ mm) of Scots pine, Norway spruce and Beech wood were modified in a N_2 atmosphere. Five residence times (0.33 – 16 h) and four treatment temperatures (190 – 245 °C) were used for thermal modification. After conditioning the modified and untreated specimens for at least six months at 65% RH, 20 °C in darkness, six properties were measured to describe its mechanical behavior, according to BS 373 (BSI 1957) and BS EN ISO 179 (BSI 1997): Janka hardness (H, n=6 per treatment), shear strength (S, n=4), compression parallel to the axis (CA, n=8), compression perpendicular to the axis (CE, n=6), Charpy impact strength (IS, n =10), and three-point bending (n=10). From the latter, MOE and MOR were obtained. Heat-induced weight loss (WL) relative to the initial oven-dry weight of the specimens, and nominal density (ND = oven-dry weight/volume at 65% RH, 20 °C) were obtained from the bending specimens; the anti-swelling efficiency (ASE, n =10) was calculated according to Hill (2006). Color coordinates of the CIEL*a*b* system were determined on the radial plane from scanned images of conditioned bending specimens prior to testing (TAPPI 1994). A cylindrical coordinate system was also tried to find out the best possible predictor of physical changes from color variables. In this, the a* and b* are substituted by the saturation C* and the hue angle h* on the colour circle around the lightness axis L* (TAPPI 1994). Data obtained from the bending specimens were deemed as representative of the full batch -each batch comprised the specimens for all mechanical tests for one treatment. For the modeling of physical properties using colour variables as predictors, simple linear regression was used. Additionally, PLS regression using the unfiltered data of the eleven colour characters (ΔE^*, ΔL^*, L^*, a^*, b^*, h^*, C^*, Δa^*, Δb^*, ΔC^* and ΔC^*_{ab}) as independent variables was carried out using SIMCA-P© software (Umetrics AB, Sweden). For constructing each calibration PLS model for MOE, MOR, ND and WL, seven specimens (out of ten) for each treatment were used, while the remaining three specimens from each treatment were left apart for the prediction set. For building each PLS model for IS, H, CA, CE, S, and ASE, mean treatment values of 14 treatments were used in the calibration set, while the mean values for the remaining 7 treatments (at 190, 210 and 230°C for 1 and 8 h, and at 245°C for 1 h) were used for the prediction set. The relative prediction error (RPE) was used to compare the efficiency of the predictions of different data sets. This was calculated as: RPE = $(SD^2 - MSEP)/SD^2$, where SD^2 is the variance of the **Y**-data in the calibration model and MSEP = $RMSEP^2$, where RMSEP = root mean square error of prediction. An RPE value close to one indicates a good prediction for specimens not included in the calibration model, while a zero or negative value suggests a poor prediction.

RESULTS AND DISCUSSION

Heating of beech, pine and spruce woods induced noticeable modifications in all colour components, mainly a decrease in L* (darkening), irrespective of the temperature of treatment (Fig. 1). Whatever the species, wood darkening deepened as the time of exposure increased, and evolved more rapidly with increasing temperatures. The rate of reduction of L* declined over time of exposure at any given temperature. This profile is similar to that of WL in TMW, and presumably manifests the chemical and colour stabilization of TMW upon increased lengths of heat treatment.

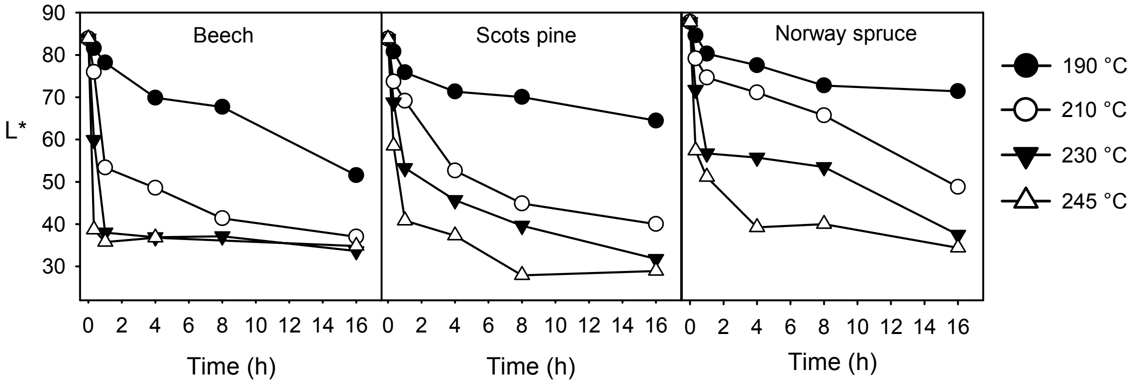

Figure 1: Lightness evolution in thermally-modified wood. Each symbol is the mean value of n=10

In all the three species, a* and b* increased at the beginning of the treatment at any processing temperature, except for beech treated at 245 °C. After reaching a maximum, both a* and b* declined with longer exposure. An increase in the temperature resulted in an acceleration of this increase-decrease cycle (plots not shown). The L*a*, L*b* plot shows that both b* and a* varied in a similar parabolic pattern with the decrease in lightness (Fig. 2a). Regardless of the species, the coordinates reach their maxima at L* = 60 for a* and at L* = 72 for b* although the evolution of the a* and b* coordinates in beech is less prominent than in the softwoods at equivalent values of L*. The direction of colour modification in the a*, b* quadrant was not-linear (Fig. 2b). Wood becomes redder and more yellow (*i.e.* more orange) as the treatment increases, and then the chromatic values decrease to reach almost zero and the wood specimens became essentially hueless. The description of the colour evolution is therefore better explained as an orange darkening towards dark grey in the three wood species. Total color difference (ΔE*) was found similar in the three woods at any given level WL and to be highly influenced by the behavior of ΔL* (Fig. 2c). Moreover, ΔE* appeared not to be linked to the schedules leading to comparable WL in each species.

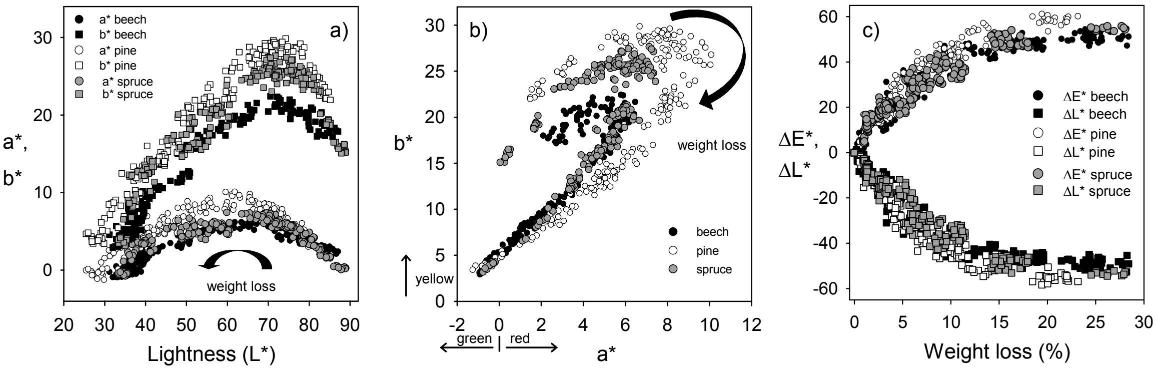

Figure 2: a) change of a and b* with the change in L*; b) the a*, b*quadrant; c) ΔE* and ΔL* in function of the WL (%) for three thermally-modified woods at 180 – 245° C for 0.33 – 16 h*

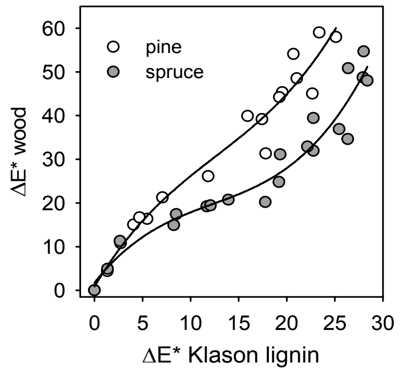

Figure 3: ΔE in TMW vs. ΔE* in Klason lignin for modified softwoods at 180 – 245° C for 0.33 – 16 h*

The total color difference (ΔE*) in wood was found to be closely, though non-linearly associated to the ΔE* in Klason lignin in treated pine and spruce woods (Fig. 3). In beech this relationship was curvilinear, but the data shows a larger scatter than in softwoods (plot not shown). Regardless the species, colour differences in lignin accounted for 40% or more of ΔE* in wood at WL > 7 – 8%. It is therefore surmised that ΔE* in TMW originates from chemical changes in the main wood polymers, especially in the lignin, due to the darkening of the lignin itself. At lower WL, polysaccharides (and extractives) possibly have a larger involvement in the colour changes of TMW.

Figure 4 represents the MOR of Norway spruce wood plotted against ΔE* or ΔL*, as an example of the nature of the relationship borne between mechanical strength and colour parameters in TMW. Table 1 presents the results of the simple linear regression to estimate seven mechanical strength parameters plus ND, WL and ASE using ΔE* or ΔL* as predictors. An examination of Table 1 shows that all models were at least very significant ($p < 0.01$). Both ΔE* and ΔL* have similar prediction ability based on the R^2 statistic, although ΔE* was better predictor than ΔL* for most physical properties.

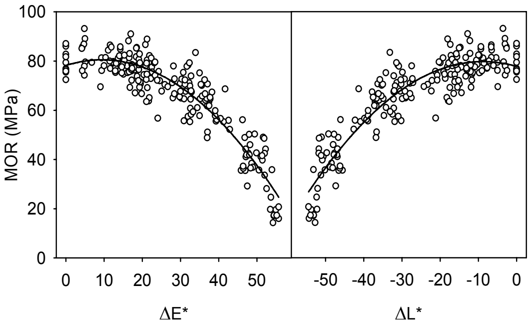

Figure 4: The relationship between MOR and ΔE and ΔL* in modified spruce wood*

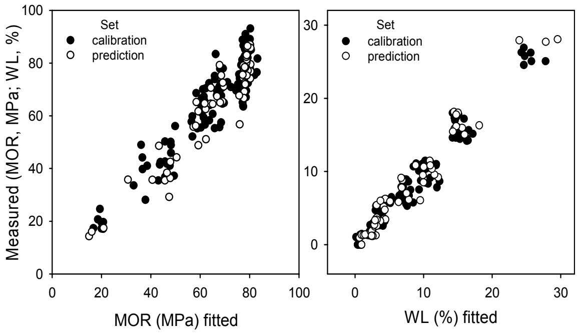

Figure 5: The fitting ability of color variables by PLS regression in modified pine wood

Table 1: Regression analysis to estimate physical parameters of TMW using ΔE or ΔL* as predictors*

Species	Response	Predictor	R^2	F (sig.)[a]		b0	b1	b2	Std. error	n
Beech	MOR	ΔE*	0.740	562.7	***	129.75	-------	-0.026	16.0	200
		ΔL*	0.726	523.7	***	129.90	-------	-0.028	16.4	200
	MOE	ΔE*	0.242	31.4	***	11,549	109.40	-2.542	1,434	200
		ΔL*	0.221	27.9	***	11,616	-106.20	-2.595	1,454	200
	H	ΔE*	0.918	201.4	***	5,532	-------	-0.974	314	20
		ΔL*	0.910	182.9	***	5,545	-------	-1.047	328	20
	S	ΔE*	0.728	48.2	***	11.46	-------	-0.0012	0.81	20
		ΔL*	0.709	43.9	***	11.46	-------	-0.0013	0.84	20
	IS	ΔE*	0.777	62.7	***	25.74	-0.427	-------	4.340	20
		ΔL*	0.777	62.7	***	25.75	0.441	-------	4.340	20
	CA	ΔE*	0.631	14.5	***	57.42	0.937	-0.018	3.27	20
		ΔL*	0.611	13.4	***	57.58	-0.968	-0.019	3.36	20
	CE	ΔE*	0.568	11.20	**	7.72	0.123	-0.003	0.71	20
		ΔL*	0.550	10.4	**	7.74	-0.128	-0.003	0.72	20
	ND	ΔE*	0.367	57.0	***	635.5	2.177	-0.061	34.20	200
		ΔL*	0.357	54.7	***	636.0	-2.265	-0.066	34.40	200
	WL	ΔE*	0.989	870	***	1.438	-0.173	0.0112	2.88	200
		ΔL*	0.884	747	***	1.465	0.196	0.0123	3.09	200
	ASE	ΔE*	0.925	220	***	-5.608	1.310	------	7.10	20
		ΔL*	0.915	193	***	-5.415	-1.346	------	7.55	20
Scots pine	MOR	ΔE*	0.820	958.6	***	117.07	-------	-0.019	10.2	210
		ΔL*	0.810	889.4	***	116.63	-------	-0.021	10.5	210
	MOE	ΔE*	0.367	60.0	***	12,443	101.30	-2.180	1,103	210
		ΔL*	0.347	55.1	***	12,535	-103.00	-2.350	1,120	210
	H	ΔE*	0.403	12.8	**	1,758	-------	-0.088	125	21
		ΔL*	0.389	12.1	**	1,755	-------	-0.093	126	21
	S	ΔE*	0.340	9.8	**	6.05	-------	-0.0004	0.58	21
		ΔL*	0.333	9.5	**	6.04	-------	-0.0004	0.58	21
	IS	ΔE*	0.879	138.4	***	27.56	-0.396	-------	2.70	21
		ΔL*	0.862	118.6	***	26.84	-0.394	-------	2.89	21
	CA	ΔE*	0.727	24.0	***	38.19	0.519	-0.010	2.04	21
		ΔL*	0.715	22.5	***	38.56	-0.544	0.011	2.08	21
	CE	ΔE*	0.555	11.20	**	4.12	0.050	-0.001	0.28	20
		ΔL*	0.551	11.0	**	4.14	-0.054	-0.001	0.28	20
	ND	ΔE*	0.277	39.6	***	513.0	1.156	-0.029	21.90	210
		ΔL*	0.266	37.5	***	513.5	-1.211	-0.032	22.00	210
	WL	ΔE*	0.932	2,854	***	0.640	------	0.0052	1.59	210
		ΔL*	0.919	1,177	***	1.370	0.060	0.0066	1.73	210
	ASE	ΔE*	0.936	279	***	-4.444	1.136	------	5.47	21
		ΔL*	0.944	318	***	-2.829	-1.147	------	5.14	21
Norway spruce	MOR	ΔE*	0.864	658.1	***	78.16	0.492	-0.026	6.5	210
		ΔL*	0.853	600.6	***	77.69	-0.455	-0.026	6.8	210
	MOE	ΔE*	0.515	109.8	***	9,208	78.82	-2.098	783	210
		ΔL*	0.504	105.1	***	9,266	-78.11	-2.136	792	210
	H	ΔE*	0.429	14.3	**	1,795	-6.02	-------	110	21
		ΔL*	0.437	14.7	**	1,774	5.68	-------	109	21
	S	ΔE*	0.807	79.5	***	6.96	-------	-0.0006	0.27	21
		ΔL*	0.795	73.6	***	6.91	-------	-0.0006	0.28	21
	IS	ΔE*	0.937	283.9	***	23.57	-0.413	-------	1.69	21
		ΔL*	0.921	221.4	***	21.97	0.383	-------	1.89	21
	CA	ΔE*	0.687	19.7	***	35.03	0.624	-0.013	2.45	21
		ΔL*	0.680	19.2	***	35.84	-0.619	-0.013	2.47	21
	CE	ΔE*	0.644	16.30	***	4.37	0.046	-0.001	0.35	21
		ΔL*	0.618	14.6	***	4.45	-0.042	-0.001	0.36	21
	ND	ΔE*	0.309	93.1	***	371.5	------	-0.012	15.80	210
		ΔL*	0.307	92.0	***	370.4	------	-0.011	15.80	210
	WL	ΔE*	0.910	2,097	***	0.580	------	0.0070	1.97	210
		ΔL*	0.899	1,847	***	1.221	------	0.0068	2.09	210
	ASE	ΔE*	0.921	223	***	-8.228	1.251	------	5.77	21
		ΔL*	0.935	271	***	-3.839	-1.179	------	5.26	21

[a] Model significance: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$; models of the form: $y = b0 + b1 \cdot x + b2 \cdot x^2$. All coefficients significant at $p < 0.05$; for property abbreviation, see text. Properties with n= 20, 21 are for mean values per treatment. Units: MOR, MOE, CA, CE, S = MPa; IS = kJ m^{-2}; H = N; WL, ASE = %; ND = kg m^{-3}

On the other hand, PLS regression improved significantly the estimation of most properties studied (Table 2, Fig. 5). The largest improvements compared to linear regression according to the R^2_Y statistic, with gains in R^2 from 6.8% to 26.6%, were for MOE and CA in the three species, IS, CE and S in beech and pine, and ND in pine. Moreover, all predictions using specimens not used for building the calibration PLS models were excellent irrespective of the species concerned. In summary, our results highlight the potential of predicting several physical properties using data of the heat-induced color evolution and color changes for small specimens of modified wood.

Table 2: Summary of statistics for PLS calibrations and predictions for physical properties of thermally-modified beech, Scots pine and Norway spruce woods from 11 colour variables

Species	Response	n	Mean	Std. Dev.	A	R^2_Y	Q^2_{CUM}	RMSEC	RMSEP	RPE
Beech	MOR	200	93.03	31.07	3	0.795	0.773	14.24	13.29	0.82
	MOE	200	11,526	1,668	3	0.359	0.325	1,350	1,214	0.47
	IS	20	9.88	8.59	4	0.982	0.947	1.40	3.71	0.81
	H	20	3,862	1,110	2	0.962	0.949	238	384	0.88
	CA	20	61.73	4.86	4	0.885	0.764	2.02	4.32	0.21
	CE	20	7.75	1.03	2	0.834	0.752	0.46	0.86	0.30
	S	20	9.30	1.61	2	0.863	0.811	0.65	0.67	0.83
	ND	200	621.3	43.2	1	0.339	0.325	35.23	31.83	0.46
	WL	200	11.58	9.03	2	0.939	0.939	2.24	2.06	0.95
	ASE	20	43.92	25.08	2	0.973	0.949	4.49	6.98	0.92
Scots pine	MOR	210	92.99	24.42	2	0.823	0.817	10.34	8.81	0.87
	MOE	210	12,779	1,435	3	0.475	0.438	11	1,066	0.45
	IS	21	13.96	8.30	3	0.970	0.940	1.65	1.91	0.95
	H	21	1,639	183	1	0.489	0.375	136	100	0.70
	CA	21	41.18	4.20	2	0.795	0.717	2.07	2.17	0.73
	CE	21	4.38	0.44	2	0.635	0.507	0.29	0.27	0.62
	S	21	5.48	0.70	1	0.458	0.397	0.54	0.66	0.11
	ND	210	511.6	25.9	3	0.374	0.323	20.70	22.56	0.24
	WL	210	7.02	6.02	2	0.958	0.957	1.25	1.17	0.96
	ASE	21	34.99	21.94	2	0.964	0.937	4.53	5.30	0.94
Norway spruce	MOR	210	66.56	17.42	3	0.876	0.873	6.19	6.30	0.87
	MOE	210	9,364	1,110	2	0.585	0.561	720	638	0.67
	IS	21	10.73	6.82	2	0.959	0.932	1.49	1.77	0.93
	H	21	1,607	156	2	0.431	0.214	128	74	0.77
	CA	21	39.17	4.92	3	0.936	0.791	1.43	0.84	0.97
	CE	21	4.33	0.60	1	0.630	0.528	0.38	0.32	0.72
	S	21	6.27	0.68	2	0.821	0.679	0.32	0.22	0.90
	ND	210	361.3	19.8	2	0.274	0.257	16.94	12.70	0.59
	WL	210	7.31	6.44	3	0.946	0.944	1.52	1.58	0.94
	ASE	21	30.79	21.51	2	0.928	0.882	6.27	3.81	0.97

n, total samples tested. Properties with n = 20, 21 are for average values per treatment. A, dimension of the calibration model; R^2_Y, explained **Y**-matrix variation by the calibration model (goodness of fit); Q^2_{CUM}, cumulative predicted variation of the calibration model (goodness of prediction); RMSEC, root-mean-square error of calibration; RMSEP, root-mean-square error of prediction; RPE, relative prediction error. Units as in Table 1.

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