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Effects of extractives removal on the performance of clear varnish coatings on boards

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Abstract

In this work, the effects of extractives removal on the performance of used varnishes were studied. The experimental samples were prepared using defect-free alder (*Subcordate alnus*) and ironwood (*Zelkova carpinifolia*) with moisture content of 12% and were coated with polyester and two-part polyurethane (urethane alkyd) varnishes. Removal of extractive materials followed Tappi Test Methods using hot water and ethanol. Variable parameters were based on the solvent type (extraction method), wood species, and varnish type. Other parameters such as moisture content, sanding process, and dimensions were kept constant. Pull-off adhesion and dynamic absorption tests were used to assess adhesion and performance of the two clear varnish coatings. Sanding process was employed prior to coating, which helped prepare surfaces virtually free of damage. In general, the extractive-free samples had better adhesion strength and wettability compared with the untreated (control) ones. Based on the results of this study, it can be pointed out that all the variable parameters, including the type of wood, varnish, and solvent, had significant effect on the adhesion of varnishes, applied on the wood surface. The difference in wettability between extracted and unextracted samples is due to blocking of the free hydroxyl groups by extractive materials. In addition, it was found that the removal of extractives had the effect of increasing the surface wettability of both species, an important consideration for the varnish coating. The highest adhesion was obtained from polyurethane varnish, applied on ironwood specimens. It seems that the diffuse-porous anatomical structure of ironwood along with its high density of 0.79 g/cm^3 could be responsible for its higher adhesion strength than alder species.

Keywords

Polyurethane, adhesion, pull-off test, varnishes, wettability

Introduction

Solid wood species are extensively used in furniture and cabinet manufacture, in which the finish plays an important role in the overall quality and service life.[1] The finishing processes have a great importance for technical, economical, and aesthetical evaluation of the wood-based products.[2] Wood surfaces coated with varnishes/paints can be protected from certain adverse conditions such as photochemical degradation, dimensional changes, biological deterioration, and fire.[2,3] The quality of the finish is a function of various parameters including application method, finish type, wood species, and surface quality of the substrate. Unless these parameters are optimized, it is very difficult to have a finished product with high quality. Surface chemistry of the substrate can be considered as one of the major properties influencing the level of adhesion between the finish and the base unit.[4] The adhesive forces between the coating and the wood surface are generally small due to the limited intimate contact created by the roughness of the surface. One of the most common

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approaches to enhance film durability is changing the chemical composition of wood surfaces. However, the most efficient chemical treatments for wood surfaces are relatively expensive and hazardous.[5]

All species of wood and other plant tissues contain small to moderate quantities of chemical substances in addition to the macromolecules of cellulose, hemicellulose, and lignin.[6] To distinguish them from the major cell wall components, these additional materials are known as the extractive components, or simply "extractives". They can be extracted from wood by means of organic solvents such as methanol, dichloromethane, acetone, and others. Extractives content in most temperate and tropical wood species are 4–10% and 20% of the dry weight, respectively. A wide range of different substances is included under the extractive heading: flavonoids, lignans, stilbenes, tannins, inorganic salts, fats, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectins, mucilages, gums, terpenes, starch, glycosides, saponins, and essential oils. Extractives occupy certain morphological sites in the wood structure.[7] Many woods, contain extractives that are toxic to bacteria, fungi, and termites; other extractives can add color and odor to wood. Generally, the presence of extraneous materials in the woody material reduces compatibility and adhesive strength of varnishes. For this reason a raw material with little or no extractive content is usually the most desirable.

From an application point of view, the present study aims to evaluate the effect of the removal of extractives, soluble in hot water and ethanol, on the pull-off adhesive strength and wettability property for two common varnishes, namely polyester and polyurethane used. Alder and ironwood were selected as the wood species for the research experiments. The investigated wood species were clearly distinguishable by differences in their physical and morphological properties. Two significant factors were taken into consideration when choosing these species. The first was that these species are widely used in the furniture and parquet sectors in Iran. The second was that they represent different anatomical structures. Alder was chosen to represent ring-porous trees and ironwood was chosen to represent diffuse-porous trees (Figure 1).

Materials and methods

Wood materials

Two wood species were used in this study: alder (*Subcordate alnus*) with an average density of 0.44 g/cm^3 and ironwood (*Zelkova carpinifolia*) with an average density of 0.79 g/cm^3. The wooden samples were randomly obtained from the northern part of Iran. A total of 60 tangential boards (30 for each species) were prepared from the latewood part. These samples should have sound surfaces, without reaction wood, knots, spiral grain, decay, and fungal infections. Air-dried samples were cut to nominal dimensions of $210 \times 110 \times 30$ mm. Then, the samples were kiln-dried until moisture content reached 10%. After conditioning, the samples were knife-planed to final dimensions of $200 \times 100 \times 25$ mm. Then, they were sanded with 120 and 180 grit (on Norton scale) sandpapers. It is to be noted that for the extractive-free samples, the sanding process was done after the extraction.

Removal of extractives

The removal of extractives was determined following the standards outlined in the TAPPI Test Methods. The procedure for the ethanol solubility followed T 204 cm-97 and hot water solubility were determined by T 207 cm-99.

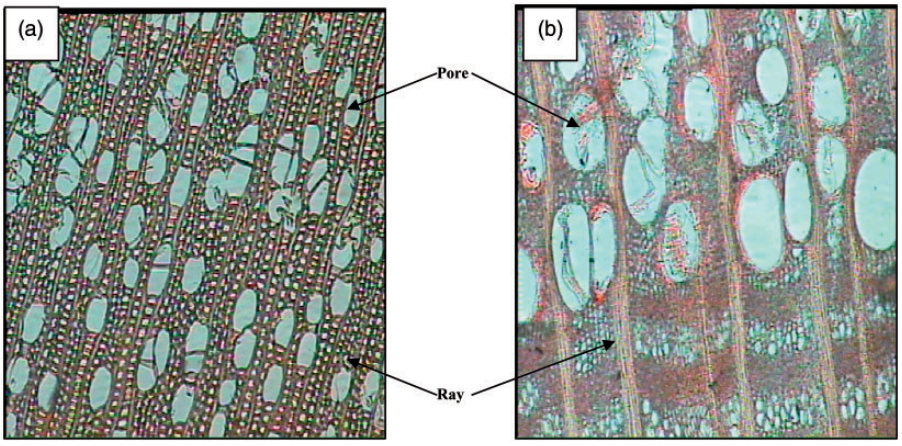

Figure 1. Cross sections of the used (a) alder (diffuse-porous) and (b) ironwood (ring-porous), magnification × 40.

Ethanol procedure

The 60-mesh sawdust sample (2 g) was placed in a Soxhlet apparatus. Extraction was performed using ethanol (250 mL) for a total period of 6 h, allowing reflux and siphoning from the Soxhlet at least 4 times per hour. Once this step was completed, the excess solvent was removed from the tea-bags by suction and washing with ethanol and then air-drying in order to remove the remaining trace of ethanol. The fully extracted samples were air-dried; initially for 48 h and then oven-dried for 24 h at $105 \pm 3^{\circ}$C. The extractive content was determined by measuring the weight loss after extraction on an oven-dried (o.d.) weight basis.

Hot water procedure

A weighed sample of air-dried 60-mesh size fiber (10 g) was transferred to a flask and hot distilled water (100 mL) was added. The flask was placed in a boiling water bath. After 3 h, the contents of the flask were transferred to a tared filtering crucible, and the liquid removed by suction on a filter flask. Then the sample was washed with hot water (200 mL) and dried to constant weight. Finally, the hot water extractive content was calculated using equation (1)

$$s = \left[\frac{(A - B)}{A}\right] \times 100 \quad (1)$$

where

A = o.d. weight of the test specimen before extraction, g

B = o.d. weight of the test specimen after extraction, g

Varnishing

In this research, solvent-based polyester and two-part polyurethane (urethane alkyd) varnishes were used. The varnishes were obtained from local market. Some of the properties of the varnishes used in the tests are given in Table 1. In varnish applications, ASTM D 3023 (1998) specifications were followed, while the suggestions of the manufacturer were also taken into account for hardener and thinner mixture ratios. One filling and two top layers of the varnishes were applied by spray gun. During application and drying, temperature was $20 \pm 2^{\circ}$C and the relative humidity (RH) was set to $65 \pm 5\%$. A filling layer was applied to the samples for the application of both varnishes. The amount of surface application was approximately 250 and 120 g/m^2 for polyester and polyurethane varnishes, respectively. The operation was made parallel and across to the grain and the samples were left to dry for 24 h.

Table 1. Typical properties of commercial varnishes used.

Varnish	pH	Viscosity (cp)	Density (g/cm^3)	Solid material (%)
Polyester	3.8	132	0.96	37.7
Polyurethane	4.5	120	0.95	25.0

Adhesion measurement

The adhesion of the varnish films was evaluated by means of a pull-off test according to ASTM D 4541 (1995). Varnished and dried samples were conditioned at $23 \pm 2^{\circ}$C and $50 \pm 5\%$ RH for a period of 16 h according to ASTM D 3924 (1996). A Posi Test AT$^+$ pull-off tester with maximal capacity of 8 MPa and $\pm 1\%$ full-scale accuracy was employed. Small 20-mm diameter dollies were glued on the film surface with a two-part epoxy resin with no dissolving effect on varnish layers. The resin was used at the rate of 150 ± 10 g/m^2 as specified in ASTM D 4541 (1995). After 24 h of curing at room conditions, the perimeters of the glued dollies were carefully incised in order to prevent propagation of failures out of the tested area. A cylindrical actuator connected to a hydraulic pump was placed over the dolly head. Vacuum was applied gradually into the actuator with a rate inferior to 1 MPa/s until separation of the dolly. The drag pointer of the pressure gage displayed the value of the pull-off strength at the rupture. The tests were carried out at 20°C and 40% RH conditions. The adhesion (X) was calculated in terms of MPa using the equation (2)

$$X = \frac{4F}{\pi d^2} \quad (2)$$

where

F = the rupture force (Newton)

d = the diameter of the experiment cylinder (mm)

Surface wettability test

Wetting analyses were performed within 24 h after surface treatments with a PG-X + imaging goniometer at room conditions of 23°C and 50% RH. Small droplets (2 μL) of distilled water were added to the treated wood surfaces with an injection micro-syringe. A frame grabber recorded the changes in droplet profile during wetting. Contact angles of droplets were measured at 1-s intervals until complete spreading. All measurements were carried out with a view parallel to the orientation of wood fibers. Two replicates were performed on each specimen. The initial contact angles θ_i, recorded

immediately after droplet deposition, were used to estimate the wood surface energies by the Berthelot's combining rule.[8] The surface tension of water was considered as being 72.8 dynes/cm.[9] In order to quantify the water spreading and penetration, the k-value proposed by Shi and Gardner[10] was calculated for each treatment condition. The time taken to complete surface wetting by water was also recorded.

Statistical analysis

Statistical analysis was conducted using SPSS software program version 22. In the analysis, the values of factor effects based on the wood type, varnish type, and extractive method were determined as a result of multiple variance analysis (ANOVA). All statistical calculations were based on 99% confidence level.

Results and discussion

Adhesion strength

In general, statistical analysis showed that the adhesion strength of the boards was significantly influenced by the varnish type, extractive method and wood species (Table 2). However, the interactions of above-mentioned variable parameters were not significant. Table 3 shows that the highest adhesion was obtained with two-part polyurethane varnish while the lowest was obtained with polyester varnish. For the type of the wood, the ironwood gave the highest while alder gave the lowest adhesion. All extractive-free boards coated with polyurethane had the highest values among the other types of specimens. In addition, for the solvent type, the adhesion strength of samples extracted with ethanol was more than those treated with hot water.

As mentioned earlier, the highest adhesion was obtained with two-part polyurethane while the lowest one was obtained with the polyester varnish. It is possible to discuss that this highest adhesion polyurethane varnish completes its polymerization reaction on the wood surface, making chemical bonding with wood, which creates a stronger adhesion on the surface. Low adhesion strength of the polyester varnish is in good agreement with that reported by Budakci and Cinar.[11] As a result of analyses, it is stated that the adhesion of polyester varnish is less than that of the two-part polyurethane varnish. It is thought that the acid value of the polyester varnish (pH 3.8) had an effect on this result. According to the acid-base theory, the changes in acidity of the substrate affect the adhesion.[2] Furthermore, in another study, it was stated that the polyester varnishes are weaker than the organic solvent varnishes regarding the hardness, brightness, and adhesion to the surface.[12]

During the adhesion tests, some parts were broken off from alder samples which were processed with polyester varnishes. This could have occurred due to low adhesion of varnish molecules and wood material or the high penetration of varnish molecules because of molecular cohesion of alder.[13] In experiments, it was seen that the failure occurred in the interface of the wood material and filling coat. Therefore, it is possible to argue that the top-layer coating has no effect on the adhesion strength.

In terms of wood species, the highest adhesion strength was obtained with ironwood, while alder boards gave lower adhesion strengths. There are a lot of factors that may cause this difference among the species, e.g. density, cell structure, basic and secondary compounds of wood, texture, extractive substances.[14]

Table 2. Analysis on variances on the effect of solvent type (A), wood species (B), varnish type (C), and their interactions on adhesion strength.

Source of variations	Df	Adhesion strength			
		SS	MS	F	SL
A	3	52.136	17.379	53.512	[a]
B	1	7.197	7.197	22.162	[a]
C	1	14.91	14.911	45.915	[a]
A × B	3	2.24	0.748	2.303	ns
A × C	3	0.94	0.314	0.968	ns
B × C	1	0.69	0.696	2.144	ns
A × B × C	3	0.028	0.009	0.029	ns
Error	16	5.196	0.325		
Total	32	1849.7			

Df: degree of freedom; MS: mean of squares; SS: sum of squares; F: F value; SL: Significance level; ns: not significant.
[a]Significant difference at the 1% level.

Table 3. Effects of extractives removal and varnish type on the adhesion strength.

Treatments	Strength (MPa)	
	Ironwood	Alder
Ethanol + Polyurethane	10.2 (0.8)	7.2 (0.6)
Hot water + Polyurethane	9.3 (0.7)	6.5 (0.5)
Ethanol + Polyester	8.1 (0.6)	5.9 (0.5)
Hot water + Polyester	7.8 (0.4)	5.2 (0.6)
Unextracted + Polyurethane	7.7 (0.7)	5.1 (0.4)
Unextracted + Polyester	6.9 (0.6)	4.4 (0.8)

A possible explanation for superior adhesion strength of ironwood might relate to the diffuse-porous anatomical structure along with its high density (0.79 g/cm^3).

Wettability

The contact angles presented in Figure 2 were the arithmetic mean of three individual measurements for each sample. In general, the wettability of samples prepared with extracted wood was observed to be higher than those made with unextracted wood. As expected from the nature of the used solvents, the ethanol-extracted samples had better wettability than the hot-water extracted ones. There appeared to be a general trend of improvement in wettability properties with the amount of extractives removed for both alder and ironwood samples

In addition to the surface energy and chemical properties of the surface, roughness influences the contact angle. High surface roughness increases large contact angles ($\theta > 90^\circ$) but decreases small contact angles ($\theta < 90^\circ$). Figure 2(a and b) illustrates a reduction in contact angle during the 2 s after the application of a droplet on the surface of the samples. Table 4 shows the effect of solvent type on the removal of extractive materials. As it can be seen, ethanol could remove more amounts of extractives. It is to be noted that the ethanol extractable content of most woods consists of waxes, fats, resins, phytosterols, low-molecular-weight carbohydrates, salts, and even some water-soluble substances.

Table 4. The effect of solvent type on the removal of extractives.

Ironwood	Alder	Solvent
Ethanol (wt%)	6.2 (1.3)	8.7 (2.0)
Hot water (wt%)	5.4 (1.7)	7.6 (1.9)

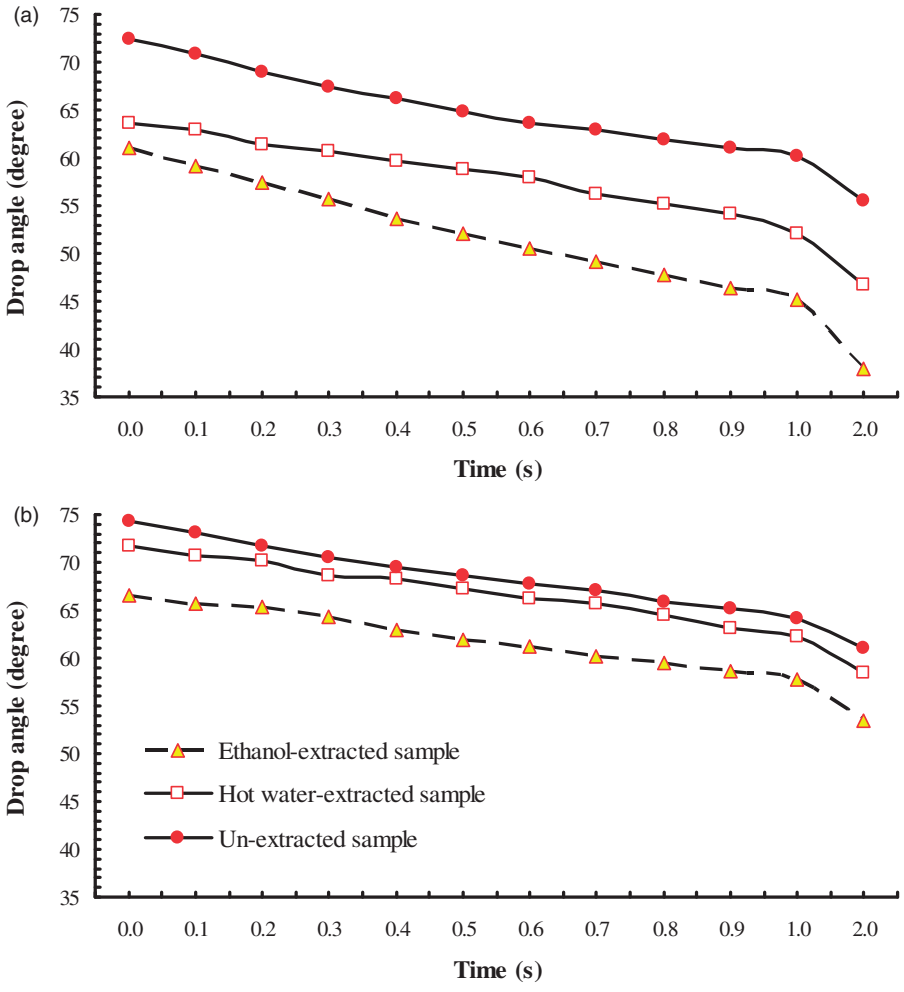

Figure 2. Wettability properties of (a) ironwood and (b) alder as a function of time.

Hot water removes a part of non-lignocellulosic components of wood, such as inorganic compounds, tannins, gums, sugars, and coloring matter present in wood.[7]

Conclusions

The objective of this research work was to investigate the effects of extractives removal, wood species, and the varnish type on the adhesion and wettability. The results presented and discussed in this study generally demonstrated that the adhesion and wettability properties were more affected by all variable parameters. In summarizing the results, the following conclusions may be drawn:

(a) In general, the largest improvement in the adhesion strength and wettability of samples was achieved when extractive materials were removed.
(b) Statistical analyses showed that the adhesion strength of the experimental boards was statistically meaningful at 99% confidence level. However, the adhesion was not significantly influenced by the interactions of variable parameters.
(c) ANOVA results clearly exhibited that samples coated with polyurethane lacquer had significantly higher adhesion strength than those coated with polyester varnish.
(d) The removal of hot-water extractives showed less improvement in the adhesion and wettability properties than the removal of ethanol extractives.
(e) In this study, the highest adhesion was obtained from ironwood, which was treated with ethanol and coated with polyurethane varnish.
(f) The poorer wettability performance for the unextracted samples may be due to the presence of more extractives on the wood surface (such as wax, fats, coloring matter, and so on) compared to the extracted samples.

Declaration of Conflicting Interests

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