

Performance of Water-repellent Treated Wooden Bath by Contact Angle Analysis

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Abstract: This study is designed to measure the durability of a water-repellent, which is used for treating a wooden bath or bathroom exposed to soapy water. Sometimes, the wooden bath is exposed to hot and alkaline water for long periods of time. The durability of the water-repellent is measured by examining the changes surface free energy by contact angle, chemical variation by FT-IR and surface morphology by SEM, hot water temperatures and varying lengths of exposure to alkaline conditions. For the specimen treated by water-repellent, according to the result obtained from contact angle analysis, the surface of sample was found to be non-polar. After dipping in alkaline liquid, the polarity of the surface of the sample increased with increasing dipping time. Therefore, the contact angle for diiodomethane, being a non-polar liquid, exhibited little change. In the test using low alkaline conditions, the water-repellent showed no chemical or mechanical surface variation for 7 days at pH 7 and at a temperature of 80°C. In the test using highly alkaline conditions, the water-repellent exhibited a change in its surface polarity value at pH 13. However, in spite of the change in its surface polarity value, the durability of the water-repellent remained constant. The results of the FT-IR and SEM tests showed no variation in the chemical and mechanical properties of the surface of the water-repellent, which was subjected to low alkaline conditions for a period of 7 days and at a temperature of 80°C.

Keywords: water-repellent, wooden-bath, durability, contact angle

Introduction

Interest in renewable resources is increasing worldwide due to increasing concerns about lack of resources and energy shortages. Wood is the only construction material that is readily renewable and it is energy efficient in its production, processing and use. Previously, quality had to do with the process of selection more than with the manufacturing process. However, wood scientists found ways to improve the wood properties by the application of various kinds of treatment. Today, new wood materials can be created, which have properties that are more precisely tailored to specific purposes. Improvements in wood properties are now a mainstream subject, extending not only to processing but also to genetics and forest management.

With the increase in the standard of living, the more prosperous consumers who are health conscious, are increasingly turning to natural wood-based materials (plywood, fiberboard and particleboard) in place of steel or chemical products, as construction materials for interior decoration and floorings.

Today, wood is used extensively in the joinery industry, for example for doors, windows and frames, as well as for log cabins, wood frame houses and other outdoor wood structures. In addition, wood can be used for baths and bathrooms. An improvement in the durability of wood coating systems such as stains, preservatives and paints has contributed to this improvement in wood properties.

Wood is a complex material, and its wettability depends on many factors: e.g. wood species, type of wood (sapwood or heartwood), previous history such as exposure to water, light, weathering or biological attacks and method of drying, grain orientation and aging of

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exposed surface [1,2].

Moreover, wood as a complex composite material has a heterogeneous, rough and even porous surfaces. There have been many studies on contact angle hysteresis phenomena [3-12] and Johanson and Dettre confirmed that a hysteresis is always present [4]. The major causes for contact angle hysteresis include roughness and chemical heterogeneity of the surface [5,13] but also other reasons are stated in the literature [14]. In general, the problem of contact angle hysteresis is not solved. The study of contact angle on a rough surface is difficult, because the problem of defining roughness is a complex one [10]. Trying to solve this problem, surface roughness factors like the Wenzel roughness factor [3] have been used. However, there is also some criticism on this concept [8]. Other attempts have been performed on paraffin wax as a model surface [9] or using purely mathematical concepts [11]. However, as all the mentioned difficulties are subject to discussion even on less complex materials, the separation of the different effects for wood is impossible up to now.

In addition, color monitoring is of great importance when wood is submitted to the processes of conservation or restoration. In general, the products used in the different treatments (consolidation, water-repellents, etc.) should not alter the surface aspect of the treated wood to any considerable extent. Variations in color can be easily detected and, therefore, the suitability of a given treatment agent can be assessed by the extent to which it alters the color of the surface treated. Accordingly, it is of great importance to monitor possible variations in color deriving from the treatment employed [15].

Water repellents (WRs) and water-repellent preservatives (WRPs) are penetrating wood finishes that increase the durability of wood by enabling the wood to repel liquid water. This ability to repel water is imparted by a wax, an oil or a similar water-repelling substance. By repelling water, WRs and WRPs enable wood to resist decay and discoloration by wood-decay fungi, which need moisture to live. The addition of a fungicide to the water repellent, which converts the WR to a WRPs, further enhances the effectiveness of the finish by inhibiting the growth of mildew and decay fungi. Water repellents and WRPs also decrease the swelling and shrinking that lead to cracking and warping. They protect painted wood from blistering, cracking and peeling.

The object of this study is to estimate the durability of the water-repellent, which is used for wooden baths or bathrooms considering that wooden baths and bathrooms are exposed to hot water as well as to alkaline conditions resulting from soapy water. Wooden baths are sometimes exposed to hot and alkaline water for long periods of time.

In this study, the durability of the water-repellent

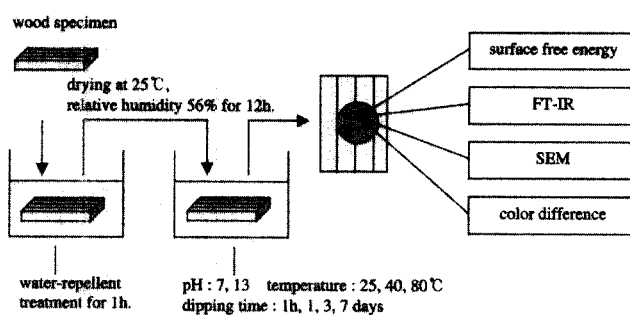


Figure 1. Schematic diagram of experimental apparatus.

was measured by examining changes in surface free energy by contact angle analysis, chemical variations by FT-IR and surface morphology by SEM, at different hot water temperatures and different times of exposure to alkaline conditions.

Experimental Procedure

Water-repellent Treatment

The specimen selected was red pine (*Pinus densiflora* S. et Z.) with an annual ring arrangement exhibiting regularity. The size of the panels was 100 mm × 50 mm × 12 mm (length × width × thickness) and the moisture content of the specimen was about 12.1% for which the specific gravity was 0.60. The specimen was prepared by rough sawing and then the surface was sanded to make it smoother. However, a few samples were left in the rough sawn state in order to investigate the effects of the surface texture.

The water-repellent treatment was a dipping for 1 h at room temperature. The water-repellent used was a silicone emulsion type (S 2-9034, Dow Coring® Co.). The solid content of the water-repellent was about 16.7%. After dipping treatment, the specimen was dried at 25°C and at relative humidity 56% for 12 h.

In this study, we estimated the durability of a water-repellent, which is used for wooden baths or bathrooms, and which is therefore exposed to hot water and to alkaline conditions resulting from soapy water.

Therefore, we made a comparison between pH levels 7 and 13, for various dipping temperature conditions of 25°C, 40°C and 80°C for 1 h, 1 days, 3 days and 7 days, respectively, as shown in Figure 1.

The pH level was controlled by sodium hydroxide (NaOH). After treatment, the specimen was stored at constant temperature of 25°C and at relative humidity 56% for at least a week prior to contact angle testing.

Contact Angle Measurements

Calculation of Surface Free Energy

It is generally agreed that the measurement of contact

angle on a given solid surface is the most practical way to obtain surface energies [16]. The theory of the contact angle of pure liquids on a solid was developed in terms of the Young equation:

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL} \quad (1)$$

Where γ_L is the experimentally determined surface energy (surface tension) of the liquid, θ is the contact angle, γ_S is the surface energy of solid and γ_{SL} is the solid/liquid interfacial energy. The most important advance represented by geometric and harmonic mean approach, acid/base approach and equation of state methods, is the introduction of a combining rule which, invoking molecular consideration and theories of intermolecular forces, eliminates γ_{SL} from Young's equation [15]. Since detailed descriptions of the underlying theory have already been published, only the most important equations are given.

Geometric and Harmonic Mean Approach or Two Liquid Method

Proposed by Wu and widely accepted, the intermolecular energy between two materials results from the summation of a dispersion component and a polar component [17]. Since the surface free energy (or surface tension) is proportional to the intermolecular energy, the surface free energy γ , itself, can be considered as a sum of a dispersion component γ^d and polar component γ^p . The interfacial energy (γ_{SL}) between a liquid and a solid polymer can be evaluated through the harmonic mean equation [3] as follows:

$$\gamma_{SL} = \gamma_S + \gamma_L - (4\gamma_S^d \gamma_L^d) / (\gamma_S^d + \gamma_L^d) - (4\gamma_S^p \gamma_L^p) / (\gamma_S^p + \gamma_L^p) \quad (2)$$

or the geometric mean equation (2):

$$\gamma_{SL} = \gamma_S + \gamma_L - 2((\gamma_S^d \gamma_L^d)^{1/2} + (\gamma_S^p \gamma_L^p)^{1/2}) \quad (3)$$

It was found that the surface energy values on three different solid polymers using harmonic mean, geometric mean and equation of stated approach, are dependent on the liquids used for contact angle measurement. In order to obtain reliable values for surface free energy from geometric and harmonic mean equations, pairs of polar and non-polar liquids have to be used [18].

The contour of a drop from an image captured by means of a video camera was calculated through an image analysis system. The contact angle (SEO 300 A, Surface & Electro-Optics Corp., Korea) was measured on each of five drops of liquid placed on a sample. The temperature during measurements was $23 \pm 1^\circ\text{C}$ and the relative humidity was $55 \pm 3\%$. In order to determine the surface

Table 1. Surface Free Energy Components of Probe Liquids

erg/cm ²	Diiodomethan (CH ₂ I ₂)	Distilled water (H ₂ O)
Surface energy (γ)	50.80	72.80
Dispersive (γ^{LW})	50.80	21.80
Polar (γ^{AB})	0	51.00
Acid (γ^+)	0	25.50
Base (γ^-)	0	25.50

free energy, the acid-based theory and two liquids method were used. The contact angle components of these probe liquids to be used in the study are given in Table 1. The liquids used for surface free energy measurements were distilled water and diiodomethane.

FT-IR Analysis

Real-time FTIR spectroscopy was used to study the chemical variation of the water-repellent. Spectra were recorded in attenuated total reflection (ATR) using a Bio-Rad FTS 60 spectrometer and a single reflection diamond ATR unit (Golden Gate, Graseby Specac). The spectrometer was set to a temporal resolution of 70 ms at a spectral resolution of 4 cm^{-1} .

In order to investigate chemical variations, we compared non-treated dipping conditions with strongly alkaline conditions at high temperature.

Scanning Electron Microscopy (SEM)

A scanning electron microscope (JEOL Japan JSM-840A) was used to study the surface morphology of the water-repellent treated wood, which was dipped in hot and alkaline conditions.

Color Difference

The surface color difference (ΔE) was measured by using a Brightmeter Micro S-5 (Technidyne Co. in USA). Color definition is based on three dimensions: hue, chroma (saturation), and lightness. Chromaticity includes hue and chroma, specified by two chromaticity coordinates. The lightness factor must also be included to identify the color of the sample with precision. For two colors to be equal, the three parameters defining a color must be equal. In 1931, the CIE defined the tristimulus values (X, Y, Z). However, the color system recommended by the CIE in 1976 (L, a, b) provides a more equally spaced system [19].

The CIE further improved upon the Hunter L, a, b, color space system producing the CIE L*, a*, b* system which is known as STARLAB or CIELAB. The CIE L*, a*, b* conversion equations for illuminant C are shown below:

$$L^* = 116(Y/100)^{1/3} - 16 \quad (4)$$

$$a^* = 500[(X/98.073)^{1/3} - (Y/100)^{1/3}] \quad (5)$$

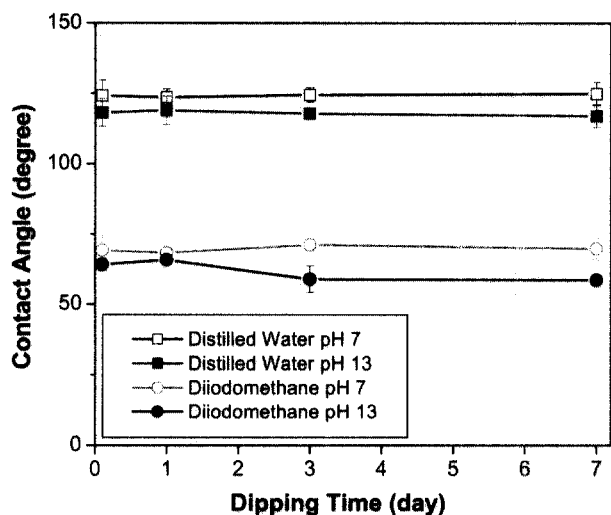


Figure 2. Contact angles by dipping time at 25°C.

$$b^* = 200[(Y/100)^{1/3} - (Z/118.232)^{1/3}] \quad (6)$$

L is the lightness variable. a and b are the chromaticity coordinates. The equations defining the system (L, a, b) with respect to the former one (X, Y, Z), taking into account two possible sources of illumination standardized by the CIE, are as follows:

$$\Delta E^*_{ab} = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (7)$$

Results and Discussion

Surface Free Energy

Because of intermolecular attractions, the molecules at the surface of a liquid are attracted in ward. This creates a force at the surface, which tends to minimize the surface area. If the surface is stretched, the free energy of the system is increased. The free energy per unit surface area, or the force per unit length on the surface, is called the surface energy.

Figure 2 presents the contact angles of distilled water and diiodomethane at pH 7 and 13 with increasing dipping time at 25°C, respectively.

After comparing pH 7 with pH 13 at 25°C, the contact angles were found to be similar in both cases. Because of the difference in surface tension between distilled water and diiodomethane, their contact angles appear to be different.

As shown in Figure 3, the contact angles of distilled water at pH 7 do not vary with increasing dipping time. However, the contact angles of distilled water at pH 13 sharply decreased over a period of one day and then gradually decreased with increasing dipping time. The contact angle of distilled water at pH 13 was affected by alkali. However, no effect was observed on the contact angle of diiodomethane at 40°C.

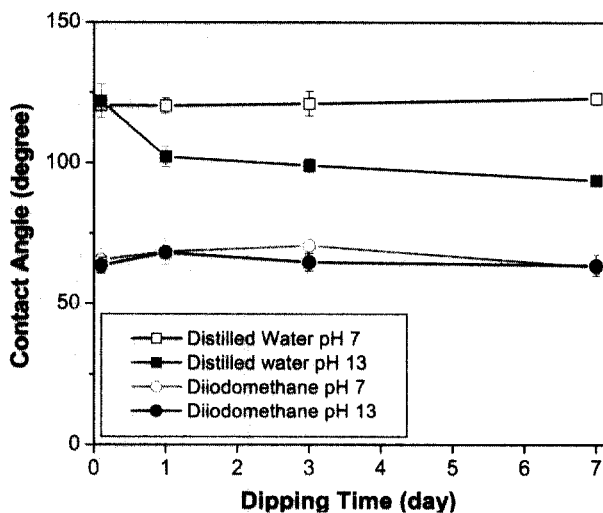


Figure 3. Contact angles by dipping time at 40°C.

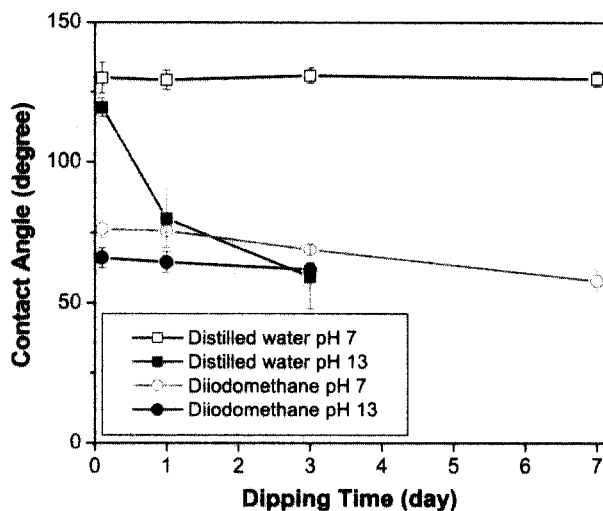


Figure 4. Contact angles by dipping time at 80°C.

As shown in Figure 4, the contact angles of distilled water at pH 13 sharply decreased with increasing dipping time, but the contact angles of distilled water at pH 7 were constant.

In comparing the case of pH 7 with that of pH 13 at 80°C, due to the effect of the alkali, the contact angles of the distilled water show a large difference.

Because the surface of wood sample became misshapen by alkali and temperature, contact angle measurement after 7 days dipping period was impossible. On the other hand, being a non-polar liquid, diiodomethane was not affected by alkali and temperature.

Figure 5 shows the polar / dispersive components of surface energy for pH 7 at 25°C. The polar and dispersive components of the surface energy of the dipping conditions were determined using equation (3). The results for pH 7 are shown in Figures 5 and 6 and the results for pH 13 are shown in Figures 7 and 8. The main reason for the surface energy variation is that the contact angle of

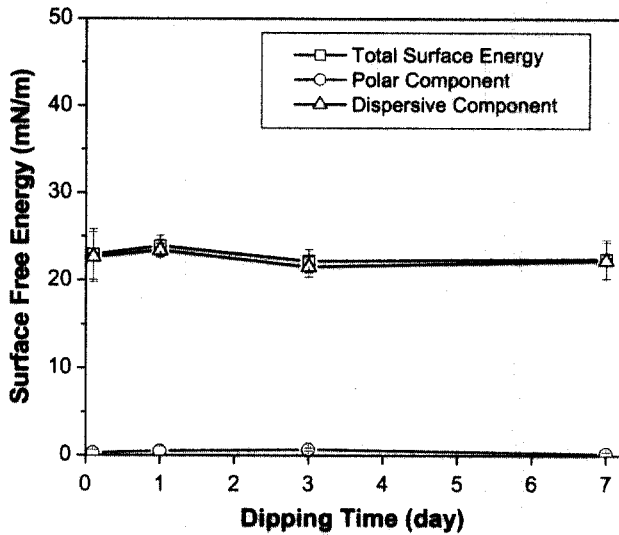


Figure 5. Polar/dispersive components of surface free energy for pH 7 at 25°C.

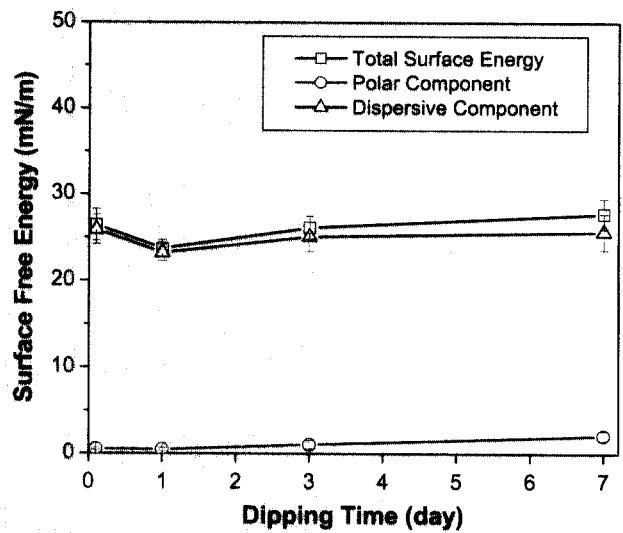


Figure 7. Polar/dispersive components of surface free energy for pH 13 at 25°C.

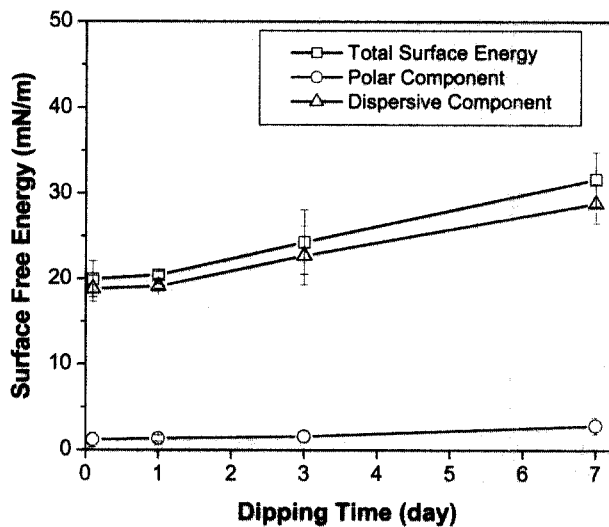


Figure 6. Polar/dispersive components of surface free energy for pH 7 at 80°C.

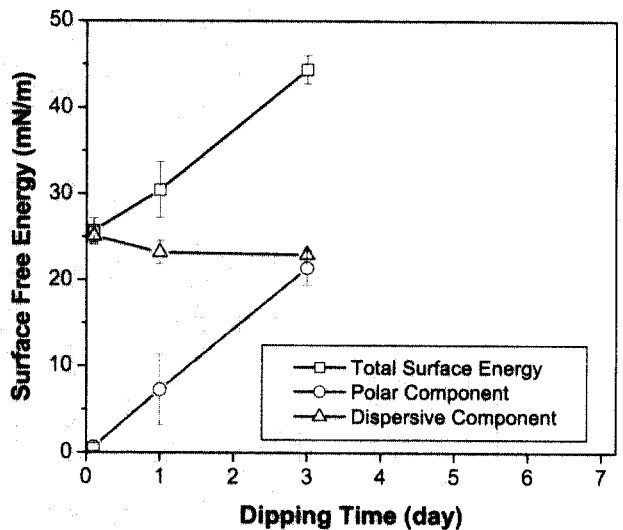


Figure 8. Polar/dispersive components of surface free energy for pH 13 at 80°C.

distilled water, which is a polar liquid, changes with pH and dipping temperature.

The contact angles varied with the liquids used and this difference in wetting is governed by two factors. One is due to the absorption of the liquids and the other is dominated by the surface acid-based interactions in agreement with the observation of Fowkes and Tischer [20]. This is because the liquids used have different chemical properties: i.e. water is known to have an H_2O structure that has an acid/base ratio of 1, while diiodomethane has a CH_2I_2 structure with an acid/base ratio of zero.

We assumed that the surface of the water-repellent treated wooden bath would be activated by some particular chemical groups. Various acid-base interactions would take place at the activated surface by the

chemical groups of pH liquids adsorbed.

Considering that the water-repellent surface, after the dipping treatment, may be rich in some particular chemical groups, these chemical groups which are present on the surface of the specimen can be expected to participate in different acid-base interactions.

Figures 9 and 10 show surface energy for pH 7 and pH 13 at 25°C, 40°C, and 80°C, respectively. As dipping temperature increases, the surface energy increases. In particular, the surface energy for pH 13 shows a marked variation with temperature.

The change in the polarity value for the surface of sample process is shown schematically in Figure 11 [21].

For the specimen treated by water-repellent, according to the results obtained from the contact angle analysis, the surface of the sample was found to be non-polar.

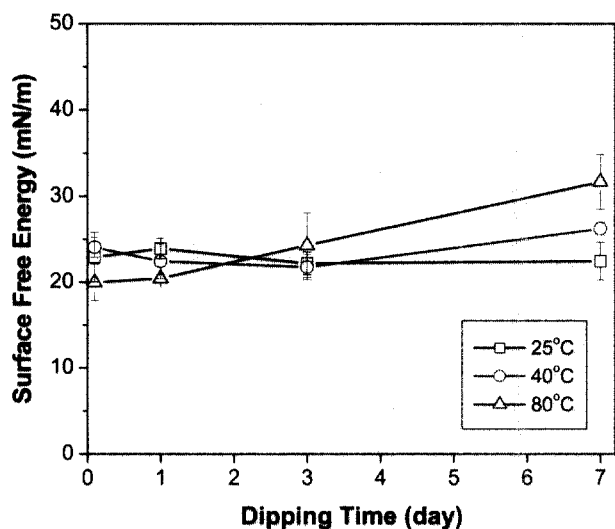


Figure 9. Surface free energy for pH 7.

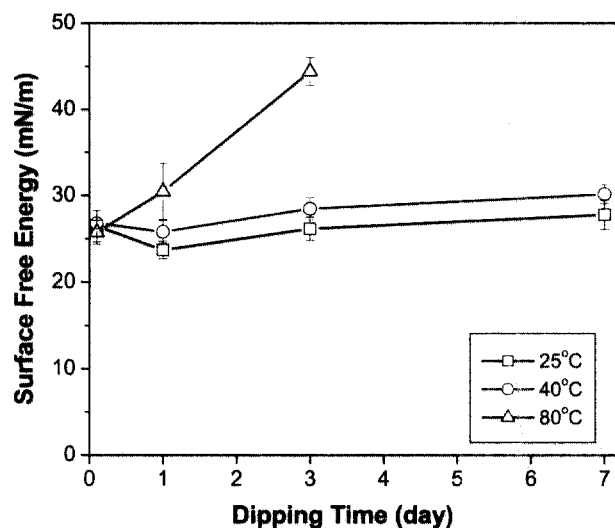


Figure 10. Surface free energy for pH 13.

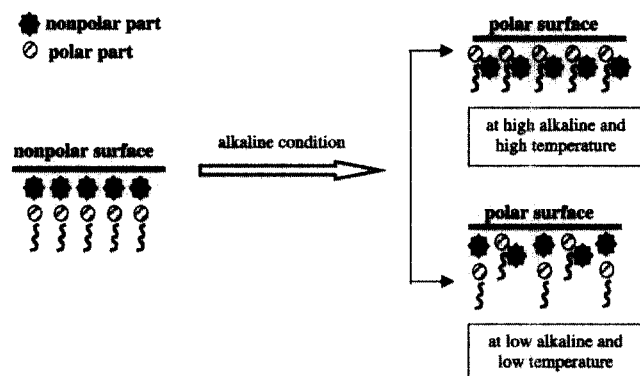


Figure 11. A schematic model of enrichment of a surface by nonpolar components containing a polar reactive functional group.

After dipping in alkaline liquid, the polarity of the surface of the sample increased with increasing dipping

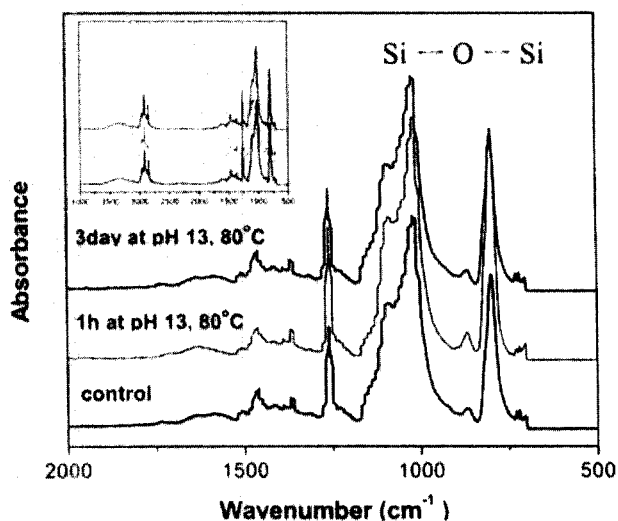


Figure 12. FT-IR absorption spectrum of water-repellent.

time. The contact angle for diiodomethane, which is a nonpolar liquid, showed only little change. However, the contact angle for distilled water, which is a polar liquid, decreased as the polarity value changed since the surface of the sample lacked stability and the surface energy increased.

The non-polar type surface increased the water-repellent component and decreased the content of the polar anhydride. This caused a nonstoichiometric ratio which tends to generate surfaces with uncured hydroxyl groups that are able to react with liquids. The measurement of the acidic and basic energy parameters of the specimen is determined from the contact angles of water and diiodomethane, respectively. It is known from Figures 5 to 8 that water has stronger acid-based properties than diiodomethane. Using equation (3) and the obtained contact angle values, the acidity energy parameter, γ_s^+ , and the associated base energy parameter, γ_s^- , of the specimen were determined. The specimen possesses an amphoteric property as was clearly revealed by the presence of an acid energy parameter, γ_s^+ , and a base energy parameter, γ_s^- . The acid energy parameter, γ_s^+ , and base energy parameter, γ_s^- , indicated an enhanced electron-donating ability and proton-donating ability of the wood surface, respectively. It was found that the specimen was weaker in electron-acceptor capability (γ_s^+) but stronger in electron-donor efficiency (γ_s^-) [22].

Fourier Transform Infrared (FT-IR)

As presented in Figure 12, Si-O-Si bonds have two characteristic IR absorption bands: the bending mode around 800 cm^{-1} and asymmetrical stretching mode around 1075 cm^{-1} , respectively. The intense band around 1075 cm^{-1} for Si-O-Si asymmetrical stretching mode is usually spread over a wave number ranging from 950 cm^{-1}

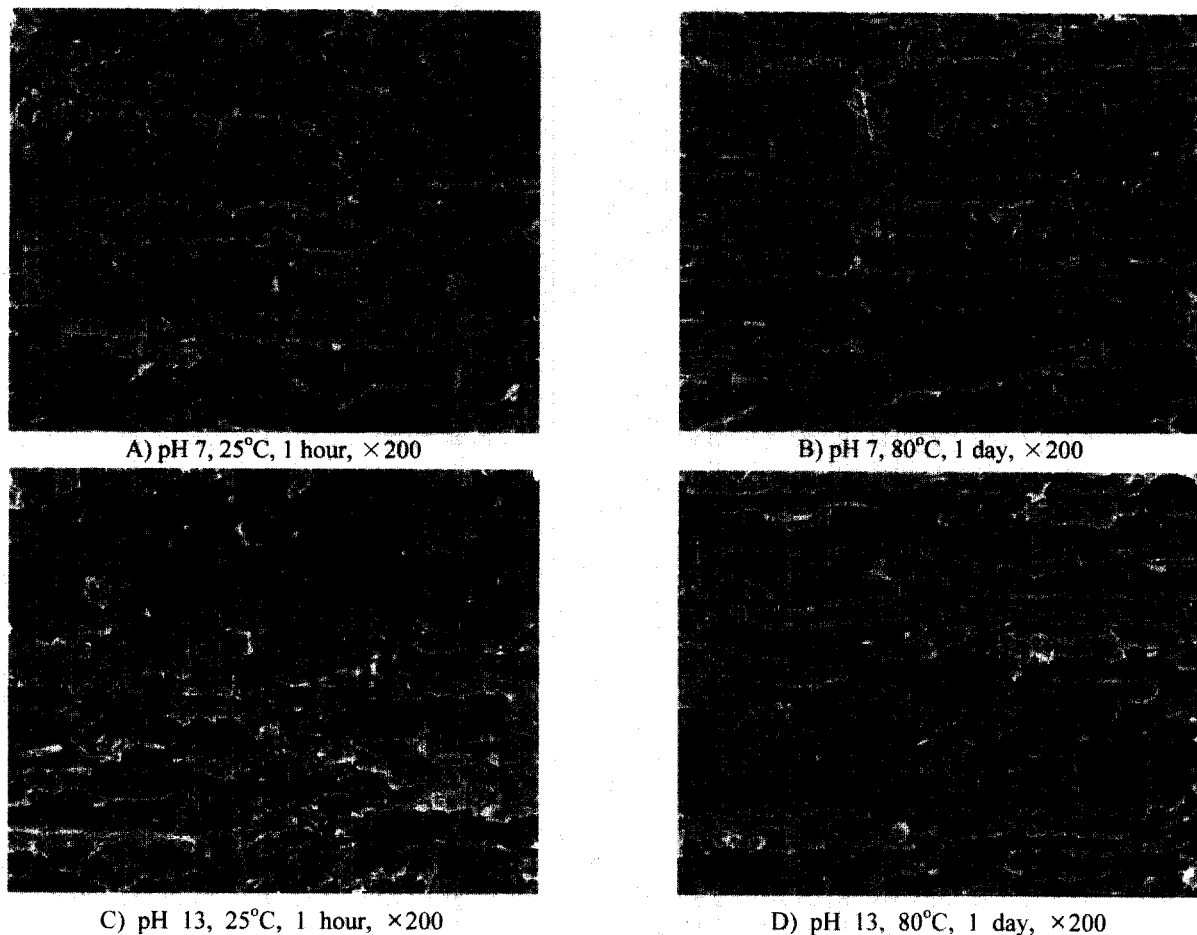


Figure 13. SEM of water-repellent treated wood surface after hot temperature and alkali condition.

to 1200 cm^{-1} , where other absorption bands such as the wagging mode of Si-CH Si around 1090 cm^{-1} - 1020 cm^{-1} , the rocking mode of SiCH_3 around $990\text{--}980\text{ cm}^{-1}$ and Si-O-C around $1090\text{--}1020\text{ cm}^{-1}$ are overlapped. It was beyond our scope to distinguish the stretching mode of Si-O-Si around 1075 cm^{-1} from all other absorption bands. Si- CH_3 bonds were well identified by an absorption band around $1260\text{--}1250\text{ cm}^{-1}$, as designated in Figure 12, which is attributed to the CH symmetric deformation in Si- CH_3 [23].

The incorporation rate of the bonds was then determined from the IR absorption intensity of the bands divided by the duration of deposition. The incorporation rate did not give any absolute values, but relative values depending on the deposition parameters since the absorption cross-section of the two bands was not available.

Comparing the spectrum for alkaline treatment (at pH 13) at 80°C with the spectrum for non alkaline treatment, little difference was observed. Therefore, the water-repellent was found to be unaffected by alkaline conditions or by temperature.

Scanning Electron Microscopy (SEM)

As shown in Figure 13, the morphology of the water-repellent treated wood surface was not affected by alkaline conditions, temperature or dipping time. As shown in the results of the FT-IR studies, the surface of the water-repellent treated wood sample remained unchanged and no damage was observed.

There is a possibility for surface cracks to appear in the water-repellent due to shrinking and swelling of the wood. No observation of the chemical variation of the water-repellent surface is found at high temperature and high alkaline conditions.

Color Difference

The data on the color coordinates were obtained from one face of the blocks. In the sample water-repellent treatment plot, it was evident that the behavior of samples at 80°C was completely different from those of the other sets of samples studied, as shown in Figure 14. At pH 7, the color difference (ΔE) for dipping temperatures of 25°C and 40°C was similar, but ΔE for 80°C suddenly dropped after 1 day. As shown in Figure 15, ΔE for pH 13 was unaffected by dipping temperature

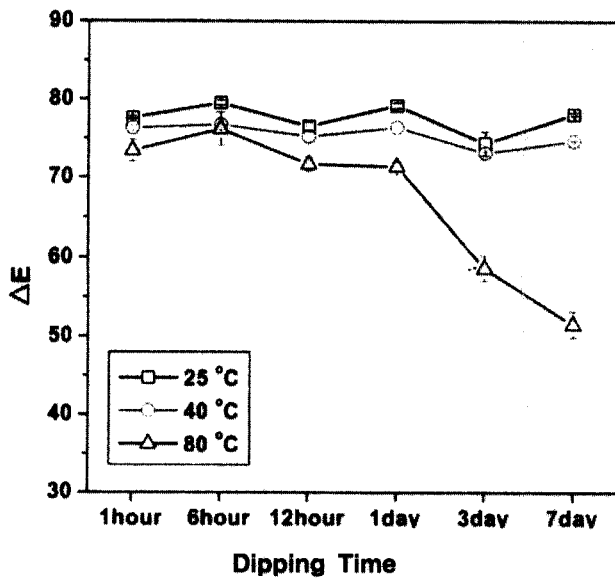


Figure 14. Color difference (E) by dipping time at pH 7.

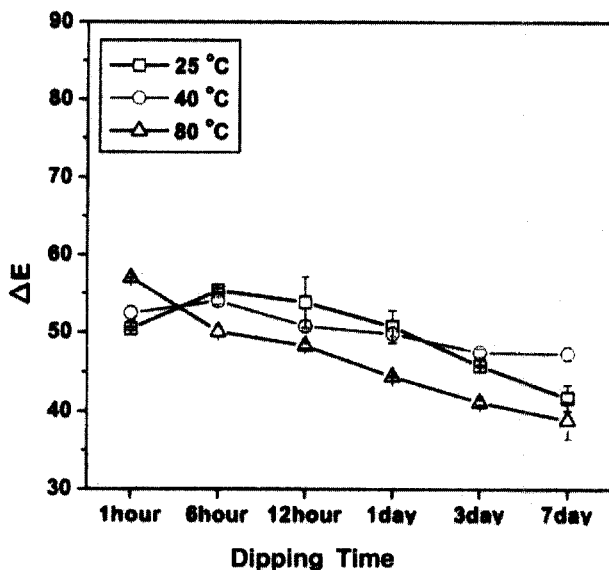


Figure 15. Color difference (E) by dipping time at pH 13.

and gradually decreased with increasing dipping time.

From the analysis of aging vs. treatment interactions, it can be seen that ΔE is lower in those samples previously aged. It seems that both aging and treatments affect the color of the samples in the same way. Of course, this depends on the intensity; so, if the color is changed by aging, the change by treatment is less than that of a similar sample that was not submitted to aging.

Among the three coordinates needed for the definition of a given color, we concluded that a direct relationship between ΔL and changes in color (ΔE) was lacking, which was different from the lightness (ΔL) showing significant variations with the other factors studied.

Conclusion

The water-repellent was coated onto wood substrates at room temperature using the dipping method. Factors affecting the chemical or mechanical durability of the water-repellent were analyzed and discussed. The durability was found to depend on the temperature used and the alkaline conditions of the wooden bath.

The durability was found to depend on the surface roughness of the water-repellent. Increasing the surface roughness decreased the performance of the water-repellent resistance.

The durability of the water-repellent was measured by means of changes in surface free energy by contact angle analysis, chemical variation by FT-IR and surface morphology by SEM, under hot water and alkaline conditions.

In the test using low alkaline conditions, the water-repellent showed no chemical and mechanical surface variation for 7 days at pH 7 and at a temperature of 80°C. In the test using highly alkaline conditions, the water-repellent showed changes in surface polarity values at pH 13. However, although the surface polarity values varied, the durability of the water-repellent maintained its performance.

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