Water-repellent coatings for surface and 3D wood processing

2015 IOP Conf. Ser.: Mater. Sci. Eng. 71 012009

(http://iopscience.iop.org/1757-899X/71/1/012009)

Water-repellent coatings for surface and 3D wood processing

N N Debelova[1], N P Gorlenko[1], G G Volokitin[1], Yu S Sarkisov[1], V P Dmitriyenko[1], E N Zavyalova[2] and P B Zavyalov[3]
[1]Tomsk State University of Architecture and Building, Tomsk, 634003, Russia
[2]National Research Tomsk State University, Tomsk, 634050, Russia
[3]National Research Tomsk Polytechnic University, Tomsk, 634050, Russia

E-mail: mackevichn72@mail.ru

Abstract. The paper presents the results of research in organic chemical compositions for hydrophobic protection of wood with the use of surface and three-dimensional coating techniques of impregnation and chemical compositions. Water absorption indicators, angles of contact on the surface of treated samples are detected herein. Kinetic equation of the moisture diffusion transition in capillary-porous structure of wood is suggested.

1. Introduction

Hydrophobic materials and coatings are substances of organic or inorganic nature. Their angle of contact exceeds 90°. These materials can be divided into two main groups: water-repellent coatings with three-dimensional impregnation capable of deep penetrating into products, and those with the surface impregnation which are applied in thin layers to the surface of hydrophilic materials thereby preventing moisture penetration. As a rule, protective properties of the latter are defined not only by the material characteristics as a whole, but by the properties and the structure of the surface layer. These coatings are applied to the surface by one or several molecular adsorptive and oriented layers. Unlike water-repellent coatings with 3D impregnation, the quality of such coatings is mainly defined by their adhesion to the product surface and resistance to the environmental factors. Water-repellent agents are practically used as low- and high- molecular organosilicon, fluor organic compounds, salts of fatty acids, surface-active agents and other compounds of organic and inorganic nature [1-3].

The aim of the present work is to study protective properties of water-repellent agents of organic nature in terms of the moisture penetration in cedar and assess the possibility of application of the suggested structures for restoration works.

2. Materials and methods

Cedar is chosen as an object of research. Cedar has density within 0.47 g/cm^3, a thin layer structure with rather narrow sapwood and high extraction of resinous substances. Cedar surface processing is carried out with a brush by application of water-repellent agent solution or fusion, while 3D cedar processing by dipping in water-repellent agent solution and their additional vacuum processing (10^{-2}atm) so as to accelerate the liquid diffusion in the volume of a capillary-porous body. The vacuum processing is carried out for several hours up to a complete gas bubble release from the sample volume. The choice of water-repellent agent for a superficial processing is conditioned by the application of compositions with chemical properties corresponding to that of the wood and thereby exerted minimum disturbance of physicochemical properties of natural wood. The work studies solutions of cellulose acetate and rosin of rather high light and weather resistance, and fusions of modified amorphous polyethylene and atactic polypropylene. The latter are wastes from petrochemical production and characterised by high adhesive strength to a wood surface [4].

3. Results and discussion

Amorphous polyethylene and atactic polypropylene are modified by oxidation of polymer fusions at 180 °C temperature. As a result, products thermal-oxidative degradation achieve the enhanced polarity and, as consequence, higher values of adhesive strength. In Figure 1, the IR spectrum is presented for amorphous polyethylene modification.

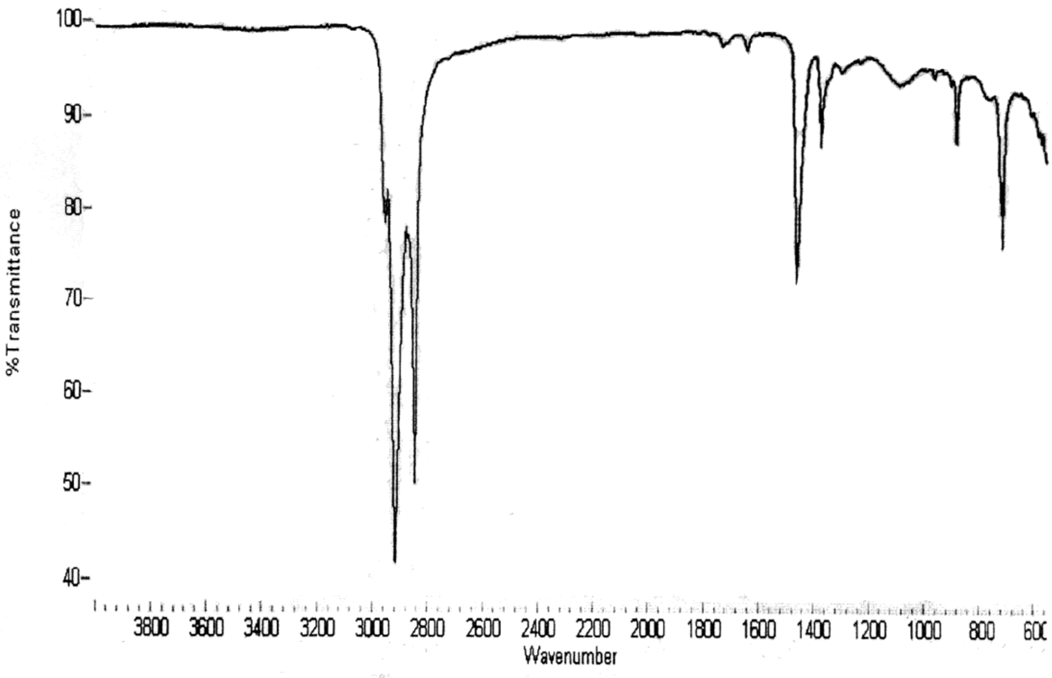


Figure1. IR-spectrums of absorption of modified amorphous polyethylene.

The analysis of curves of the IR spectrum shows that oxidizing processes run rather intensively. In comparison with the original samples, the greatest changes of absorption peaks are observed within 600–1300 cm^{-1} region. This spectrum region characterizes mainly the mixed type of chemical components of the environment. Thus, such groups as ketonic, aldehydic and ester are found in the oxidized amorphous polyethylene that interfaces with non-saturated communications.

Asymmetric ($V_{as}CH_2$) and symmetric stretch vibrations (V_sCH_2) are shown in the vicinity of 2926 and 2853 cm^{-1}, respectively. The methyl group includes two types of bending vibrations. The first type is symmetric bending vibrations at which deformation of C-H bond occurs in a sample phase. The second is asymmetric bending vibrations at which deformation of C-H bond occurs outward the phase. Symmetric bending vibrations (δ_sCH_3) occur near 1375 cm^{-1}, while the asymmetric ($\delta_{as}CH_3$) occur near 1450 cm^{-1}. Also, the intensive absorption is observed in the vicinity of 1200–1420 cm^{-1}, caused by O-H deformation and C-H stretch vibrations. These bands change their position which, however, can be determined by the high intensity of absorption. The existence of polar bond C-O causes the emergence of the intensive absorption band within the range of 1000–1200 cm^{-1} due to the contribution of this group to skeletal vibrations. Moreover, the intensive absorption bands in the region of 1250–1400 cm^{-1} are connected with planar bending vibrations of OH-group [5].

Thus, at the product modification, the quantitative and qualitative composition of polar groups is changed in the medium of oxidized amorphous polyethylene that leads to the increase of the adhesive strength and resistance to the environmental factors.

Table 1 presents experimental data on kinetics of cedar water absorption. These data show that kinetics of water absorption has the explicit induction period caused by the structural properties of cedar.

The calculation and analysis of wood kinetic curves show that the process of moisture transfer proceeds by the diffusive mechanism and can be obtained from:

$$C = a + b\times\exp(-k_1\times t) + c\times\exp(-k_2\times t), \quad (1)$$

where C is the total content of absorbed moisture; k_1, k_2 are constants of diffusion speeds, *a*, *b*, *c* are constant coefficients, (b+c) is the maximum moisture content absorbed by the sample, (b+c) is theoriginal moisture content in the sample, *t* is the time period of moisture absorption.

Table 1. Water absorption kinetics at surface cedar processing.

Water-repellentagent	Absorbed water ratio, min					
	5	10	15	20	30	3600
Cellulose acetate solution	0.01	0.01	0.01	0.02	0.04	0.35
Rosin solution	0.02	0.02	0.02	0.03	0.05	0.44
Modified atactic polypropylene	0.02	0.02	0.03	0.03	0.03	0.11
Modified amorphous polyethylene	0.03	0.05	0.05	0.05	0.06	0.21
Test sample	0.63	0.75	0.75	0.75	0.88	1.52

The kinetic equation parameters for the experiment conditions are given in Table 2.

Table 2. Kinetic equation parameters for cedar.

Kinetic parameter values				
a	b	c	k_1	k_2
34	-12	-15	-0,03	-0,05

As Table 2 and kinetic equation (1) show, the process of water absorption is characterized by two diffusion constants that means that water absorption is carried out in two ways. In authors' opinion, it is connected with the existence of capillaries and pores of different sizes and, as consequence, different speed of their filling with water.

It is known that the main indicator of the water-repellent agent efficiency is the value of the angle of contact which, in turn, depends on the surface structure of the samples. The values of the angle of contact of hydrophobic materials under study are given in Table 3.

Table 3. The contact angle of hydrophobic materials depending on the contact point between water drop and sample surface.

Water-repellent agent	Contact angle, min						
	0	5	10	15	20	30	60
Cellulose acetate solution	98	98	98	97	97	96	94
Rosin solution	96	96	96	96	95	94	92
Modified atactic polypropylene	119	119	119	119	118	117	115
Modified amorphous polyethylene	124	124	124	123	123	122	118
Test sample	34	2	0	0	0	0	0

It should be noted, that these results are obtained for a rough wood surface. It is known [6], that besides a chemical composition, the efficiency of water-repellency treatment depends on the surface texture, coating application technique, modes of homogeneous or heterogeneous wetting at which the liquid contacts with the entire surface or its part. To compare, the obtained compositions are applied to a glass substrate. As the experimental data show, the angle of contact increases by 5-10 % as compared to the rough wood surface. Since heterogeneous wetting is used for wood and homogeneous wetting for glass, the phenomena observed are considered as regular and can be obtained from [6]:

$$\cos\Theta = f\times r\times\cos\Theta_0 + f - 1, \quad (2)$$

where Θ andΘ$_0$ are angles of contact of homogeneous and heterogeneous wetting, respectively; f is the wetted surface area; $r = S_0/S$ is the roughness coefficient; S_0, $S$are true and apparent surface areas, respectively.

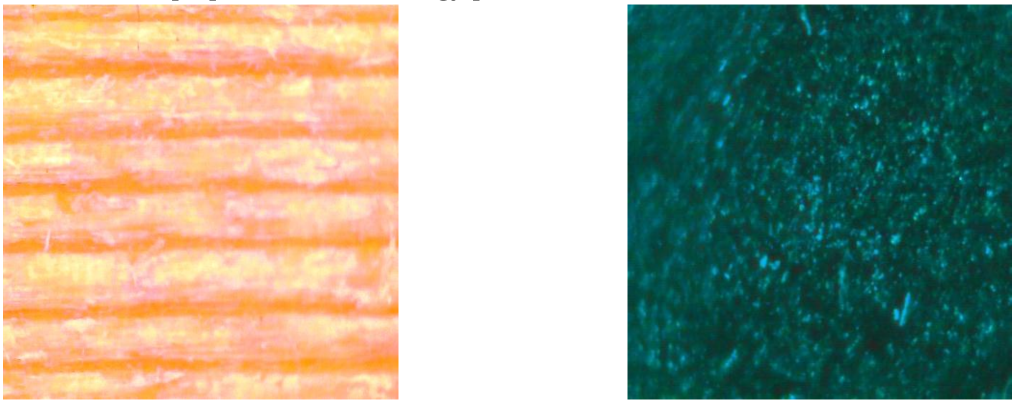
According to equation (2), in presence of the surface roughnesses and decrease of values f and r, the angle of contact also decreases. Therefore to achieve a highly hydrophobic state, it is necessary to create a specific surface texture. Different methods of creating such textures can be found in literature. One of them is a low-temperature high-speed plasma etching of a surface that leads to a formation of nanodisperse carbon having a high chemical attraction to organic wood composition.

As a result, not only a surface texture is formed, but also high operational and decorative properties, water permeability decreases, fungus diseases are eliminated, abrasion resistance increases. Moreover, the speed of surface processing is 1–2 s that reduces energy costs and improves cost efficience of the coating creating process [7]. The similar results are also observed when processing various wood surfaces using laser and radiation effects.

Figure 2 illustrates the surface topography of cedar before and after its processing with low-energy plasma.

Low-energy plasma treatment, as shown in Figure 2, eliminates the surface texture and forms closely packed dispersed carbon particles having a certain degree of crystallinity that provides the increase of hydrophobic properties of the wood surface. However, in compositions under study, the ange of contact (Θ) increases insignificantly on the pretreated surface.

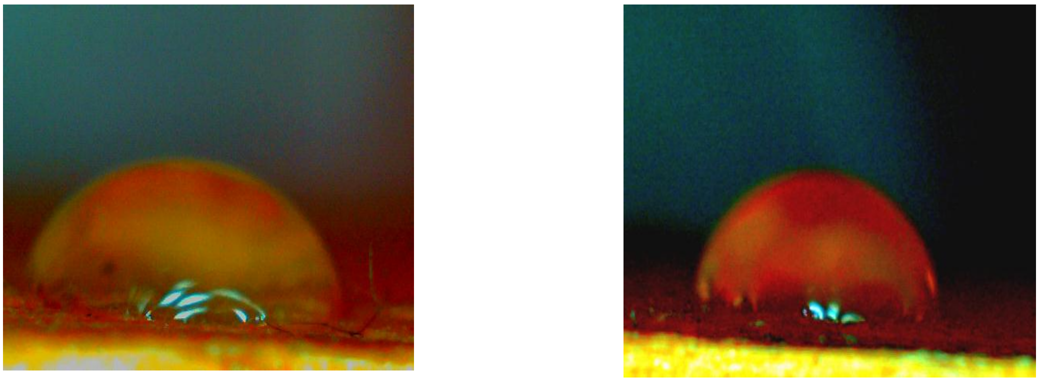
Figure 3 presents hydrophobic properties of the surface covered by the cellulose acetate solution for pure wood and preprocessed low-energy plasma.



a b

Figure 2. Micrographs ofcedar pure surface (a) and afterlow-energy plasma treatment (b).

It can be explained first, by the fact that at closely packed dispersed carbon particles, irrespective of their size, it is impossible to create highly hydrophobic surfaces [6], and, second, that layers self-organized under a high-energy effect have a plurality of structural defects affecting water repellency. Optimization of the plasma treatment process will allow elimination of these limitations.



a b

Figure 3. Microphotos of water drops on pure wood surface after water-repellency treatment (a) and pretreated with low-energy plasma (b).

Despite the small value of its density showing the maturity of the pore structure, the three-dimensional wood impregnation with water-repellent agents is not practically observed under common conditions. The maximum moisture penetration comes to fractions of millimeters. In vacuum processing, the depth of penetration in water-repellent agents increases up to several millimeters. This can be explained by a thin-layer structure of cedar, the existence of hydrophobic functional groups in the chemical composition which prevent water-repellent agent molecules from diffusion into the volume of the solid body and due to some other reasons. The effective wood impregnation at great depth is observed when using an oxalaldehyde aqueous solution. However, water-repellent properties are practically absent. In further research it is supposed to use this substance as transport for other molecules possessing water-repellent properties. A scenario when the internal pore surface is modified by groups of the similar origin while the surface by another can be thus implemented. In authors' opinion, the lesser the size of pores the stronger this effect is.

One can assume that the adsorbed layer of the water-repellent agent will be formed by immobilized molecules which have no the possibility of moving as whole, and, in practice, their random distribution will occur within the capillary-porous body. At that, water-repellent agentmolecules can be adsorbed equally possible in any region of the surface, while the angle of contact will be determined just by the nature of end groups.

4. Conclusions

1. It was shown that at a thin-layer coating with water-repellent agent of the sample surface, the values of the angle of contact range between 96 and 98°. Taking into account the chemical compatibility of the suggested compositions with wood components, they can be used while restoration of wood products.
2. It was detected that compositions based on modified amorphous polyethylene and atactic polypropylene are the effective water-repellent agents. Wood surface coating with the suggested compositions allows decreasing water absorption by several times.
3. It was shown that wood processing with oxalaldehyde aqueous solution in vacuum installation allowed the three-dimensional sample impregnation.
4. It was shown that water adsorption by wood occurred by the diffusion mechanism and was obtained from $C = a + b \times \exp(-k_1 \times t) + c \times \exp(-k_2 \times t)$.

IOP Conf. Series: Materials Science and Engineering **71** (2015) 012009 doi:10.1088/1757-899X/71/1/012009

References

[1] Семенов В В 2009 Гидрофобизация древесно-стружечных и древесно-волокнистых плит кремний-органическими мономерами и жидкостями *Химия растительного сырья* **4** 177
[2] Verchinina G S 1989 Применение кремний-органических соединений в строительстве (Москва: Мир)
[3] Под ред. Кротикова 1991 Органосиликатные и кремний-органические материалы в практике строительных, противокоррозионных, защитно-декоративных, ремонтных и реставрационных работ *Материалы научно-практической конференции* 76 с
[4] Дебелова Н Н, Горленко Н П и Подшивалов И И 2009 Технология гидрофобной защиты капиллярно-пористых строительных материалов и изделий *Вестник ТГАСУ* **2** 121
[5] Smith A 1982 *Прикладная ИК -спектроскопия* (Москва: Мир)
[6] Boynovich L B and Emelyanenko A M 2008 Гидрофобные материалы и покрытия: принципы создания, свойства и применение *Achievements of chemistry* **77** 619
[7] Volokitin G G, Volokitin O G, Shekhovtsov VV, Maslov Ye A and Malyuga N V 2010 Plasma Process Modeling of Wood Surfaces *Vestnik of TSUAB* **3** 220