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Full Length Research Paper

The effect of sea water on laminated wooden material

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In the present study, black pine samples laminated with epoxy and polyurethane glues were treated with various wood preservative chemicals and made subject to seawater for one year. The samples were examined from the point of view of physical features such as changes in odor and color as well as their mechanical values in 3-month periods. For this purpose, the samples were made subject to bending tests perpendicular to the fibers, compression tests parallel to the fibers and adhesion tests. As a result of this study, it was observed that, non-impregnated samples were excessively decayed and they were so decomposed and destroyed that they could not be used anymore within the first 6 months. It was determined that, sea insects nested on the said samples and began to live there, sea worms destroyed the wooden surfaces by drilling them, the said surfaces were covered with seaweed, the surfaces became extremely soft and there were white decays on some regions. In case of impregnated samples, very small changes occurred in odor and color and moreover, any decay was not seen. Also, significant changes were observed as a result of mechanical tests.

Key words: Bending strength, compression strength, bonding strength, black pine, lamination.

INTRODUCTION

Forests have been lessening rapidly day by day in the world as a result of rapid developments in wood works industry. Wooden material has a significant place in human beings' life. The demand for wooden material has been increasing step by step because it is easily treated, insulates heat and voice. It has a high resistance and aesthetic appearance (Ozalp, 2003). Using large and curved wooden material as a whole single piece is not very suitable regarding the economy and durability features.

Using one-piece massive wood in large carrying elements causes many problems in practice because many defects existing in the body of the wooden material (knot, decay, crack, curved fiber, wormhole etc) cannot be removed. High quality wood should be used to eliminate these defects. This will cause increases in material cost. Using a whole single wooden piece in manufacturing curved elements is not cost-efficient because it will cause increase in waste.

Lamination technique should be used for using wooden material efficiently, removing its defects and avoiding decrease in resistance in curved form manufacturing due to the diagonal fibers. Small and larger-size wooden materials can be manufactured by this method. Also, it allows removing defects from the wooden materials which results in usable products (Senay, 1996).

Wood is a building material, which is used inside sea in addition to interior and exterior use prevalently. Especially, it is used in construction of large buildings such as harbors, piers and ports as a significant sub-structure material. Moreover, it is employed in construction of sea vehicles such as boats, vessels and yachts prevalently. Especially, the fact that wood is a renewable and relatively inexpensive compared to other building materials promotes using it inside seas.

After the wooden material is started to be used inside sea, it is attacked and decayed by fungi, insects and various sea worms in a short time. Naturally hard resistant woods should be used for minimizing these attacks. However, such woods are rarely used inside sea because they are very expensive and have limited amount. Thus, wood types, which are not very resistant naturally, also are used inside sea prevalently after they are treated with various chemicals.

In the previous studies, it was evidenced that, many

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chemical materials protected wooden materials, which were used inside sea. Thomasson et al. (1988) reported that, wooden materials, which were used inside sea as building material, were decayed within a time shorter than one year and recommended that, such wooden materials were used after they were treated with suitable wood protection materials or naturally high-resistant wood types were used inside sea. Eaton (1985) reported that, naturally high-resistant wood types should be used inside sea. He also reported that, in case that, wood types, which are not very resistant naturally, have to be used inside sea, they should be protected against fungi, insects and sea worms by treating them with wood protection materials before they are used inside sea.

Johnson and Gutzmer (1984) left wooden materials treated with creosote inside sea in their study. They reported that, the non-impregnated samples were decayed in a short time like 6 - 18 months while the wooden samples treated with various chemicals continued to exist without being decayed for 13 - 14 years in the experiments.

Dickey (2003) reported that, wooden materials are suitable building materials for decks, harbors, courts' equipments and other purposes and naturally high resistant wood types should be used. He also reported that, wood preservatives are effective in increasing life-span of wooden materials and emphasized that, suitable preservatives should be preferred. In the previous lamination and mechanic studies, Eckelman (1993) recommended that, laminated wooden materials (LVL), which are aesthetic, inexpensive and have superior technological features compared with massive wooden materials, are preferred in furniture manufacturing and framework elements, which should be resistant. Demetci (1991) reported that, the type of adhesive affected adhesion resistance, tension strength parallel to fibers, compression and cleavage resistance significantly in the wooden materials produced by adhering pine, fir, beech, oak and maple coatings by PVAc and epoxy glues.

Moody (1981) used timbers from firs and southern pines in 2nd and 3rd quality class in his study done for determining compression resistance parallel to fibers of single- and double coat laminated samples made of from firs and southern pines. As a result of this study, it is evidenced that, double-coat samples are more resistant against compression than those, which are single-coat (Senay, 1996). Ibach reported that, the wooden samples impregnated with various compounds of copper and arsenic resist against sea insects inside sea.
Especially, double-impregnated samples were protected more effectively against all sea insects (Sivrikaya, 2003). Johnson (1977) observed that, CCA and ACA impregnation of woods from trees with needle-leaf with water-soluble salts provides sufficient protection against insects inside moderate and non- moderate seas (Anon, 2008).

In this study, black pine samples laminated with epoxy and polyurethane glues were treated with various wood preservative chemicals and made subject to seawater for one year.

MATERIALS AND METHODS

Wooden material

Wooden materials from Black pine (*Pinus nigra*) were employed as test material in this study. Attention was paid to prefer black pine (*P. nigra*) wooden materials, which were almost perfect, with smooth fibers, free from knots, free from diseases caused by fungi, normally grown, free from reactive woods and also free from diseases caused by fungi and insects, in choosing test materials. Test samples were prepared from live parts of the wood material.

Glues

In this study, polyurethane (PU) and epoxy glue types were employed in this study. Main objective why these glue types were chosen is the fact that, they have high resistance against water. Polyurethane glue is manufactured from an alcohol with double-bond and a suitable isocyanate. Its cohesion and adhesion forces are very high. It can resist against acids, fats, boiling water and microorganisms.

Curing time is 60 min at room temperature (20°C). The glue expands approximately twenty-fold in volume after it has completed its reaction and no shrinking occurs in the glue coat. Epoxy glue is a two-component epoxy adhesive with a mixing proportion of 1:1. Its adhesion power is very high and it does not cause shrinking. It provides a clear appearance and resists rupturing and shearing.

It dries slowly and can be formed during drying. They are employed prevalently in bonding especially, wooden materials to be used in water, electronic system parts and their insulation against water and other solutions, and bonding ceramic, concrete, metal and non-metal parts (Anon, 1990).

Impregnation materials

Protim WR 230

This impregnation material provides long-term protection because it is naturally insoluble in water. Solvent vaporizes and leaves the wooden material after impregnation process. Then, main active material remains and provides protection. It provides extremely effective protection against insects and fungi. Its density is 0.8 g/cm^3. It is inflammable at temperatures above 36°C (Ozalp, 2003).

Wolmanit-CB

It contains 35% of copper sulfate ($CuSO_4.5H_2O$), 45% of potassium bichromate ($K_2Cr_2O_7$) and 20% of boric acid (H_3BO_3). Its protection effect is well against fungi, which cause soft decays and destroy wood, insects, termites, and harmful insects, which destroy wood inside seawater (Ozalp, 2003).

Korasit KS

It is a chromium-free, and boron-free wood preservative based on Copper and ammonium salt according to German standard DIN 68800 used in wood impregnation. It is a suitable preservative for using in children's playgrounds, pergolas, fence piles, garden and city furniture for outdoor use as well as wooden materials, which are in continues contact with water and soil, such as carrying and tensioning elements in constructions, supports, roofs, coatings etc (Anon., 2006).

Table 1. Average seawater temperatures in mediterranean region (℃).

Months	January	February	March	April	May	June	July	August	September	October	November	December
Seawater temperatures (ºC)	16.4	15.1	15.8	17,1	20.6	25.3	28.4	29.3	27.8	24.8	21.1	17.9

Preparation of test samples

Laminated wooden material was prepared as 3-layer in size of approximately 20 x 70 x 920 mm from the coatings, which had completed air-drying, with a thickness of 6.66 mm according to TS EN 386.

The glue solution was applied on only one of the surfaces by brush as 180 - 220 g/m^2 according to the glue manufacturer's recommendations. The surface was left for 5 min after the glue was applied and then, placed under cold pressure with 0.8 N/mm^2 and left for 12 h under this pressure. Once the glue had cured completely, wooden samples were prepared in the sizes specified in the applicable standards.

Impregnation of test samples

Test samples, which just completed air-drying, were impregnated with Protim 230WR and Korasit-KS by pressure method. In case of impregnation with Wolmanith-CB, vacuum-pressure method was employed. Impregnation time was 3.5 h in the impregnation process with Wolmanith-CB and it was 1.5 h in case of impregnation process with Protim 230 WR and Korasit-KS.

Placing the samples on the test area

After the impregnation process was completed, the samples were so placed in plastic sacks with large pores and allowing easy water penetration that they were not overlapped and was subject to seawater under equal conditions. These sacks were housed in an iron cage for avoiding scattering because they would be left inside sea for a long time. Impregnated and non-impregnated samples were submerged inside sea 6 m below sea level on the test area of Turkey-Mersin-Erdemli, Middle East Technical University Sea Sciences Institute (34^{o}16'E 36^{o}33'50''N) and regularly checked and examined. Seawater temperatures versus months are seen in Table 1.

Test methods

Visual observation

Once the samples had been left in the test area, their positions inside sea were observed regularly once a week. Also, the samples, which were brought out of sea in 3-month periods, were made subject to a careful visual examination. After the research processes were completed, the notes were reported and the samples let back inside sea.

Mechanic tests

The samples, which were brought out of sea, were left in a climate-controlled cabin at 20℃ and 65% of relative humidity until humidity balance was received. Then, humidity was brought to 12%. Thus, humidity variations between test samples were eliminated.

Test for static bending strength

Ten samples were prepared in size of 20 x 20 x 300 mm for each test according to the requirements specified in TS 2474, static bending strength tests. The distance between the bases of the test apparatus was adjusted to 240 mm and the force was applied to the surface of the samples perpendicular to annual rings exactly at the center. 12-fold of thickness of the samples was considered in specifying the distance between the bases of the test apparatus. Loading rate was so set that breaking would occur after 1.5 - 2 min and maximum force at breaking moment was determined with a precision of 1 kp and calculated by the equation below:

$$\sigma_e = \frac{3.P.L}{2.b.h^2} \qquad (1)$$

Where; σ_e, Bending strength (N/ mm^2); P, Max. force at the moment of breaking (N); L, Distance between points of support (mm); b, Width of sample piece (mm); h, Thickness of sample piece (mm).
Bending strength test mechanism is given in Figure 1.

Adhesion test

Ten samples were prepared in size of 20 x 15 x 150 mm for each test according to the requirements specified in TS 53 and TS 2470, and they were made subject to adhesion test according to DIN 53255 (Anon, 1981; Anon, 1964). Tensioning rate was so set that delamination would occur after 1.5 - 2 min parallel to fibers and maximum force at delamination moment was determined with a precision of 1 kp and calculated by the equation below:

$$\sigma = F / A = F / (bxl) \qquad (2)$$

Where; σ, Bonding strength (N/mm^2); $F_{max,}$ Max. force at the moment of breaking (N); b, Width of bonding surface (mm); l, Length of bonding surface (mm).

Bonding strength test mechanism is given in Figure 2.

Compression test

Ten samples were prepared in size of 20 x 20 x 30 mm for each test according to the requirements specified in TS 2595 for compression tests parallel to grain (Anon, 1977). A constant loading was applied at precisely center of the horizontal cross-section of the samples. Loading was so set that it can smash the samples within 1.5 - 2 min. Loading was applied until the samples broke down and maximum force at the moment of the breaking was written down and calculations were done by using the following equation:

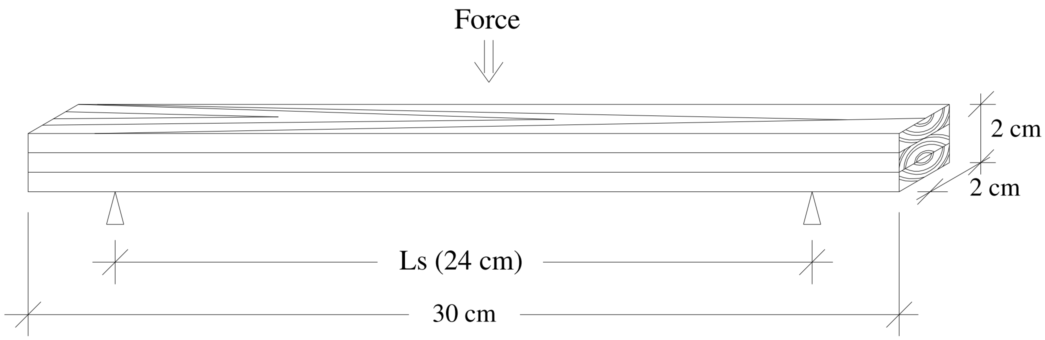

Figure 1. The dimensions of bending strength test specimens.

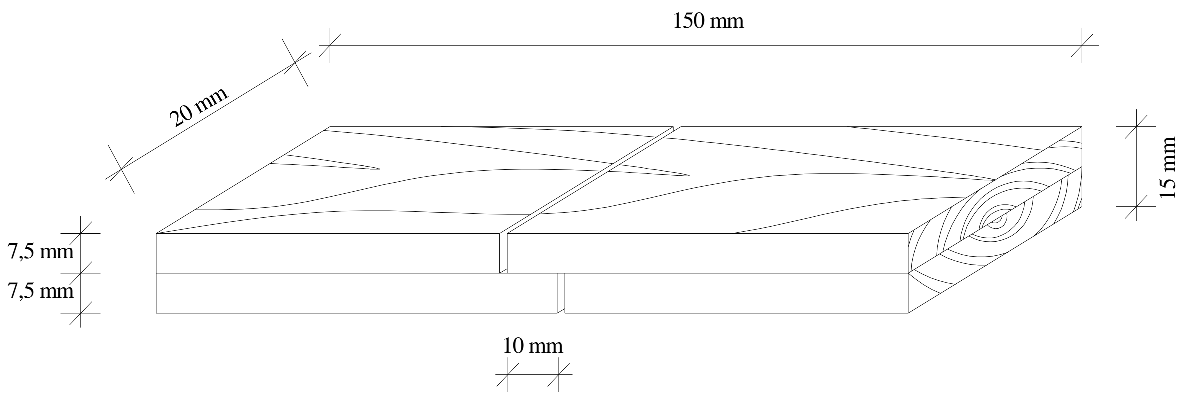

Figure 2. The dimensions of bonding strength test specimens.

$$\sigma_b = \frac{F_{max}}{a.b} \quad (3)$$

Where; σ_b, Compression strength (N/mm^2); F_{max}, Max. force at the moment of breaking (N); a, Width of sample breadth cross-section (mm); b, Length of sample breadth cross-section (mm).

Compression strength test mechanism is given in Figure 3.

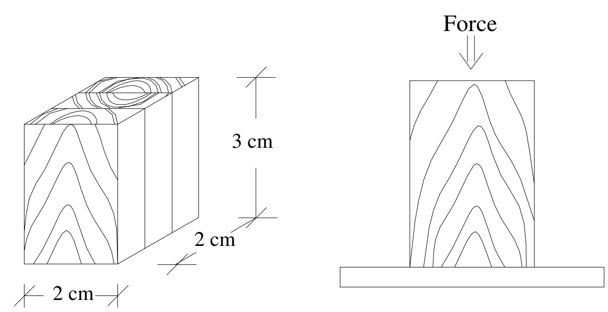

Figure 3. The dimensions of compression strength test specimens.

RESULTS AND DISCUSSION

Physical evaluations

Data were obtained as a result of careful visual examinations done in 3-month periods on the impregnated and non-impregnated samples, which were left inside sea forone year. In the examinations done on the samples brought out of sea after the first three months, it was observed that, the highest odor and color variations occurred in the non-impregnated samples and those impregnated with korasit KS (compared with their natural odor and color).

A light color became dominated in the samples, which had been impregnated with korasit after impregnation process, before leaving them inside sea. This color became more significant as the samples stayed inside sea for months. Then, it was seen that, this color became slightly dark brown compared with the initial values and it could be seen with naked eye when the samples impregnated with korasit were examined visually at the end of the first three months.

In case of the samples impregnated by Protim WR 230 and Wolmanit CB, it was observed that, a little color variation occurred initially while change in color was also very little at the end of the 3 months. From the point of view of decays, insignificant wormholes were seen in the non-impregnated samples at the end of 3 months. Sea worms made holes beginning from the surface of the non-impregnated wooden materials up to a depth of 1 - 2 mm. Also, when these samples were held by hand, it was observed that, hand slid slightly on their surfaces. However, no decay was seen in the samples impregnated by all 3 of the impregnation material.

According to the examinations done after 6 months, color variations were quite significant in case of the non-impregnated samples compared with their initial values. Dark brown became more significant. Also, when these samples were held by hand, it was observed that, sliding on the surfaces was sensed more strongly. Odor also changed highly into a severe humidity odor. From the point of view of decays, in case of the non-impregnated samples, number of the wormholes per unit square on the surface and diameters of the holes increased. Moreover, small sea crustaceans attached and nested on their surfaces. Johnson and Gutzmer (1990) reported that, the non-impregnated samples were decayed very severely by sea worms within 6 - 18 months in their study relating to sea. Even at the end of this period, any decay was not seen in any of the impregnated samples.

According to the visual examinations performed after 9 months, color and odor variations highly increased especially, in the samples impregnated with Korasit KS. However, it was observed that, color and odor variations increased in the samples impregnated with Protim WR 230 and Wolmanit CB also compared with the initial values. Color of the samples impregnated with korasit became dark brown. When the samples were examined by hand, it was observed that, their surfaces were coated with a mucous-like material. It was also observed that, cavities occurred on the surfaces of the non-impregnated samples when they were squeezed by hand. From the point of view of decays, number of the wormholes per unit square on the surface and diameters of the holes increased and also spread over the surfaces of the non-impregnated samples. Holes went to a depth of half of the thickness of the samples. Also, it was seen that, the number of the sea creature species nested on the surfaces of the non-impregnated samples increased. As a result of very careful visual examinations done on the samples brought out of sea after 12 months, it was observed that, colors of the samples especially, impregnated with korasit KS and non-impregnated samples completely changed. Natural color of the wooden materials changed into dark brown. From the point of view of odor, it was observed that, the highest variation occurred in the non-impregnated samples. When the samples were examined by hand, it was seen that, non-impregnated surfaces were scratched easily by nail and the sample was completely decayed. Mucous-like material on the surfaces increased and white decays were seen in some regions.

With respect to decays, it was seen that, wooden materials were so decayed that they could not be used anymore. Number of the holes per unit square increased and they reached the other surface of the material. Diameters of the holes ranged between 1 and 4 mm. Such holes were not seen in the impregnated samples. It was observed that, number of the sea crustaceans increased on the non-impregnated surfaces and they were coated with seaweeds. Decomposition was very severe. It was observed that, all the non-impregnated materials were so decayed that they could not be used anymore at the end of 12 months. However, any decay was not seen in any of the impregnated materials with the exception of changes in their colors and odors.

As understood from the previous studies, test materials left inside sea without any protection were decayed by sea insects within a short time. In the study done by Edwin and Ashraf (2005), severe and more severe decays occurred in the samples left inside sea for 90 and 150 days (Anon, 2008). Rao et al. (1993) reported that, the samples left inside sea without any protection were completely diminished by sea worms within a short time like 4 - 6 months. Also, Edwin and Gopalakrishna (2004) reported that, the non-impregnated samples made subject to marine conditions were diminished completely within a short time like 6 - 7 months in their study.

Mechanical results

Numeric data relating to mechanic tests are seen in Tables 2, 3 and 4. According to the results of mechanical tests, static bending test results show that, resistance increased in the impregnated samples compared with the initial values while decreases occurred in the non-impregnated samples. Because the non-impregnated samples were decayed more severely, they lost their resistance. As seen in the previous studies, losses occur in resistance of the samples, which were decomposed very severely. It was believed that, the reason why the resistance increased is the fact that, the glue line and the main active material were in contact with water and the glue line became very hard as well as adhesion and cohesion forces between smooth surfaces increased.

In the studies performed, decreases were observed in compression values in certain rates compared with the initial values. Small sizes of the samples may affect adhesion values negatively. Consequently, glue amounts in the glue lines in contact with water were small also. Then, the line was affected negatively and decreases were seen in compression values.

Considering adhesion test results, it was seen that, some values increased while others decreased. It is believed that, the reason for this situation is the fact that, wooden materials absorbed the impregnation material in different amounts and they interacted with the glue in different ways.

Yildiz et al. (2003) researched effects of some impregnation materials on the mechanical features of the yellow pine wood in their study. The samples taken from yellow pine were impregnated with the solutions at the

Table 2. Results of static bending tests performed on the samples from black pine.

		Starting (N/mm^2)					1 year (N/mm^2)				
Kind of glue	**Impregnation materials**	**Min.**	**Max.**	**ē**	**δ_x**	**n**	**Min.**	**Max.**	**ē**	**δ_x**	**n**
Polyurethane	Nonimpregnated	26.43	30.18	28.18	1.01	10	23.12	26.36	24.82	1.07	10
	Protim 230 WR	31.40	34.16	32.00	1.26	10	42.93	45.16	44.6	0.65	10
	Wolmanit CB	33.78	36.10	34.74	0.79	10	41.30	44.36	42.78	0.96	10
	Korasit KS	31.46	35.07	33.04	0.98	10	38.26	40.97	39.44	0.81	10
Epoxy	Nonimpregnated	31.60	35.19	32.28	0.94	10	25.16	28.86	26.66	1.15	10
	Protim 230 WR	31.11	33.18	31.74	0.66	10	50.98	54.16	52.63	0.89	10
	Wolmanit CB	31.96	35.80	33.60	0.93	10	52.70	55.10	53.63	0.71	10
	Korasit KS	30.10	33.20	31.73	0.75	10	46.21	48.50	47.72	0.61	10

Table 3. Results of compression tests performed on the samples from black pine.

		Starting (N/mm^2)					1 year (N/mm^2)				
Kind of glue	**Impregnation materials**	**Min.**	**Max.**	**ē**	**δ_x**	**n**	**Min.**	**Max.**	**ē**	**δ_x**	**n**
Polyurethane	Nonimpregnated	21.58	25.56	23.26	1.16	10	12.84	14.01	13.53	0.38	10
	Protim 230 WR	20.02	23.50	21.72	1.06	10	13.20	14.84	13.86	0.44	10
	Wolmanit CB	23.11	25.05	24.21	0.63	10	14.01	15.87	15.00	0.52	10
	Korasit KS	22.16	25.72	23.29	1,10	10	13.70	15.07	14.35	0.51	10
Epoxy	Nonimpregnated	24.45	28.17	26.52	1.56	10	16.08	18.56	17.15	0.73	10
	Protim 230 WR	20.18	23.50	21.41	1.12	10	15,73	16.70	16.11	0.39	10
	Wolmanit CB	22.18	25.06	23.35	0.75	10	14.78	17.08	16.22	0.72	10
	Korasit KS	20,01	25.08	22.29	1.44	10	15.19	16.49	16.03	0.36	10

concentrations of CCA 0.85, 1.5 and 2%, ACQ 1900 2, 3 and 7%, ACQ 2200 1 and 2%, Tanalith E 3491 2 and 2.8%, Wolmanith CX–8 2 and 2.8% respectively. An increase in elasticity modulus of the samples impregnated with 2.8% of Wolmanith CX–8 and 2% of Tanalith E–3491 compared with the control samples. However, they did not change or decreased in the samples treated with other chemicals. An increase was seen in bending strengths of the samples impregnated with 2.8% of Wolmanith CX-8 and 7% of ACQ-1900. However, they did not change or decreased in the samples treated with other chemicals.

Barnes et al. (1993) treated the samples taken from South America pine with CCA-C and ACQ solutions and researched elasticity modulus in their study. In case of treatment with CCA-C, retention amount was selected as 9.6 kg/m^3 and full cell method was employed. They reported that, any significant variation was not seen between elasticity modulus of the non-treated samples and those treated with chemicals and then, dried.

Bal (2006) impregnated yellow pine wooden with ammonium copper quaternary (ACQ) by using immersion and pressure methods and researched changes occurred in some physical and mechanical properties. As a result, he reported that, impregnation process with ACQ chemical did not cause statistically significant variations in mechanical characteristics of the wood. As a result of the treatments done by using immersion and full cell methods for 72 h, decreases at a level of 20% were observed in shrinking and expanding amounts of the wood.

According to Bobat (1994), wooden materials used inside sea are used by sea creatures as food and nest. Wooden materials are decayed by these harmful animals

Table 4. Results of adhesion tests performed on the samples from black pine.

		Starting (N/mm^2)					1 year (N/mm^2)				
Kind of glue	Impregnation materials	Min.	Max.	ē	δ_x	n	Min.	Max.	ē	δ_x	n
Polyurethane	Non impregnated	2.06	3.27	2.67	0.42	10	2.36	2.90	2.67	0.18	10
	Protim 230 WR	2.64	3.09	2.84	0.13	10	2.36	3.01	2.66	0.18	10
	Wolmanit CB	1.80	2.70	2.37	0.33	10	2.01	2.97	2.70	0.27	10
	Korasit KS	2.31	2.99	2.64	0.22	10	2.01	2.70	2.86	0.18	10
Epoxy	Nonimpregnated	2.26	3.06	2.58	0.27	10	1.96	2.63	2.33	0.25	10
	Protim 230 WR	1.70	2.90	2.27	0.28	10	1.71	2.48	2.03	0.19	10
	Wolmanit CB	1.50	2.70	2.08	0.31	10	1.91	2.70	2.31	0.24	10
	Korasit KS	3.20	4.05	3.56	0.29	10	2.01	2.70	2.39	0.18	10

making holes first perpendicular and then parallel to grain. Thus, sea worms cause destruction of wooden materials inside sea rather than changes. This is a different situation from decays caused by fungi and may be called as destruction.

As a result, if a wooden material is used inside sea, wooden materials from naturally resistant tree species should be preferred. However, wooden materials from tree species, which are not naturally very resistant, they should be used after treated with wood preservatives. Also, because laminated wooden materials have superior mechanical characteristics compared with massive wooden materials from the same tree species, it should be preferred especially, in cases that, good resistance and mechanical properties are desired.

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