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The Effect of Nano-Graphene on Some Surface Properties of Beech Wood Coated with Water Based Varnish

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Abstract

In this study, the effect of nano-graphene (NG) added water based varnish on the surface hardness, brightness and color change of beech (*Fagus oriantalis* L.) wood was investigated. 0.25%, 0.50% and 1% by weight of NG were added to the water-based (WB) varnish and prepared varnish solution was applied to the beech sample surfaces. According to the results, the surface hardness of the varnished samples increased compared to the unvarnished samples. However, the addition of NG does not have a significance on the increase in hardness. The brightness values of the samples decreased depending on the increase in NG added to the varnish. Moreover, the surface color of wood samples has changed significantly. It has been shown that NG can be used as a colorant to achieve a darker color in wood. It is also thought that additional studies are needed to determine the properties such as aging performance and adhesion resistance of NG-added varnishes.

Keywords: Wood, varnish, graphene, surface properties

Su Bazlı Verniklerle Kaplanmış Kayın Odununun Bazı Yüzey Özelliklerine Nano-Grafenin Etkisi

Özet

Bu çalışmada, kayın (*Fagus oriantalis* L.) odununun yüzey sertlik, parlaklık ve renk değişimi üzerine nano-grafen (NG) katkılı su bazlı verniğin etkisi araştırılmıştır. Su bazlı vernik içerisine, ağırlıkça %0.25, %0.50 ve %1 NG eklenmiş ve ardından hazırlanan çözelti kayın örnek yüzeylerine uygulanmıştır. Araştırma sonuçlarına göre, verniksiz örnekler ile karşılaştırıldığında verniklenmiş örneklerin yüzey sertliği artmıştır. Ancak, NG eklemesi sertlik artışında bir öneme sahip değildir. Vernik içerisine eklenen NG miktarındaki artışa bağlı olarak örneklerin parlaklık değerleri azalmış ve yüzey rengi önemli derecede değişmiştir. Ahşapta koyu bir renk elde etmek için NG'nin renklendirici olarak kullanılabileceği görülmüştür. Ayrıca, NG eklenmiş verniklerin yaşlanma performansı, adezyon direnci gibi özelliklerinin belirlenmesi için ilave çalışmalar yapılmasının önem arz ettiği düşünülmektedir.

Anahtar Kelimeler: Ahşap, vernik, grafen, yüzey özellikleri

INTRODUCTION

Wood material and wood composites are the most used semi-finished products in the furniture and decoration industry. These materials need to be protected due to their organic compounds and this process usually involves the coating of surface with protective layers. All organic polymers are sensitive to UV radiation and polymer concept includes structures such as lignin and cellulose. For this reason, it is known that some characteristics of wood, such as color, change rapidly when exposed to outside conditions (Vardanyan et al., 2015). Paints and varnishes are widely used to prepare protective layer in furniture and decoration members produced with wood material. Paints and varnishes that offer a wide range of values such as color and brightness are frequently used materials for aesthetic reasons as well as their protective properties.

As in the past, most of the paint/varnish consumed today is soluble in solvent-based solvents and the volatile organic compounds (VOC) in the solvents get into the air and cause serious damage to the atmosphere. In the world, certain studies have been carried out to reduce to using of VOCs since the second half of the 20th century. First, in 1955, the Clean Air Act (US EPA, 2007), which considered air pollution as a serious problem in the United States at the regional level, restricted or totally prohibited the use of certain air pollutants in some states. Later, in 1963, 1970, 1977 and 1990, the boundaries were enlarged by major changes in the related agreement. In 1997, the Kyoto Protocol was signed with the participation of many countries in the world, and a serious initiative was started worldwide to reduce the gases harming the atmosphere. Water-borne varnishes contain less volatile organic compounds than solvent-borne types due to their construction. For this reason, the use of water-based systems is becoming increasingly widespread and technologically advanced.

Water-borne systems, which taking up prominence in the paint/varnish industry, contain VOCs at much lower levels than almost all the solvent based resins. Emulsion polymerization types have been used for a long time and are preferred due to their superior properties and low VOC values (Yıldız et al., 1999).

Making various modifications to alter certain properties of the varnish is a common and preferred process. These modifications mostly include properties such as color (Vardanyan et al., 2015), hardness (Sönmez et al., 2004), brightness (Keskin and Atar, 2008), and adhesion resistance (Sönmez et al., 2004).

The Graphene, consisting of a combination of the words "graphite" and "ene", is the name given to flat layers of carbon atoms tightly knit in the form of a two-dimensional (2D) honeycomb (Geim and Novoselov, 2007). The graphene, which is currently the thinnest, strongest and most robust carbon structure known, is expected to undergo major changes in the future, particularly in the sectors of electronics, medicine, construction, aeronautics, in terms of its advanced physical and chemical properties (Bozkurt, 2015). In this study, it was aimed to determine the effect of the nano-size graphene, which was added at different ratios (0.25%, 0.50% and 1%) into water based varnish, on the surface hardness, brightness and color properties of Eastern beech (*Fagus oriantalis* L.) wood.

MATERIAL and METHOD

Wood Material

In this study, the Eastern beech (*Fagus Orientalis* L), which is also often preferred in furniture production, was used. The samples were prepared from randomly selected first grade timbers and were cut as annual rings perpendicular to the surface (radial section). It has been noted that there is no knot, crack, differences in color and density of the samples (TS 2470 1976). The samples were cut at air-dry moisture ratio in dimensions of about 550×110×12 and were conditioned at 20 ± 2 °C and 65% ± 3 relative humidity until they have reached the constant weight in the air conditioning cabinet. Subsequently, six samples (n = 6) were cut for each test variant in dimensions of 100×100×10 mm (longitudinal direction*radial direction*tangential direction). Then, the surfaces of samples were sanded with 150 and 180 grit sandpapers, respectively. Dust particles were removed with pressurized air after sanding process to make samples ready for varnishing.

Nano-Graphene Added Varnish

Samples were varnished with a one-component, glossy water-based wood varnish. To modify the water-based varnish properties, nanographene (NG) was added in proportions of 0.25%, 0.50% and 1%. Some features of used NG are given in Table 1. The varnish solution was stirred with a magnetic stirrer for 30 minutes to obtain a homogeneous solution. Technical properties of varnish solutions are given in Table 2.

Table 1: Properties of Nano-graphene

Appearance	Purity (%)	Density (g/cc)	Diameter (µm)	Thickness (nm)	Specific surface area (m^2/g)
Black	99.5	0.2-0.4	1.5	3	750

Table 2: Varnish properties

Varnish type	pH degree	Density (g/cm³)	Application viscosity (sn/DIN Cup 4mm/20 ˚C)	Amount of applied varnish (g/m²)	The amount of solid matter (%)
WB	8.1	1.02	18	80	37.75
WB + 0.25% NG	8.1	1.02	18	80	40.55
WB + 0.50% NG	8.0	1.01	18	80	40.30
WB + 1% NG	8.0	0.99	18	80	39.70

WB: Water-Based Varnish; NG: Nano-Graphene

The varnishing of the test samples was carried out in accordance with the manufacturer's recommendations and according to ASTM-D 3023. The varnish application was carried out using a soft bristle paint brush as 1 filler coat and 2 finish coats. Waited two hours between coats and the surfaces slightly sanded with 280 grit sandpaper. The amount of varnishes was weighed using 0.01g precision analytical scale. The test samples were placed in parallel to the ground plane and kept at room temperature for three weeks for complete drying.

Determination of Surface Hardness

The surface hardness of the samples was determined following to the König method with the pendulum hardness measuring device according to TS EN ISO 1522. In the testing device, which oscillates with two balls at 63 ± 3.3 HRC hardness and 5 ± 0.0005 mm in diameter, the layer hardness was measured according to oscillations between 3° and 6°. Surfaces with high number of oscillations have high hardness, while those with low oscillations have lower hardness (Sönmez, 1989). Two measurements were taken on each sample surface and the arithmetic mean was recorded as a single value.

Determination of Surface Brightness

The brightness measurements of the samples were determined in parallel and perpendicular to the grain with a gloss meter according to TS EN ISO 2813. Two measurements were taken on each sample surface and the arithmetic mean was recorded as a single value.
In determining the brightness of the paint and varnish layers, 20 ° angle for matte layers, 60 ° angle for both matte and glossy layers and 85 ° angle for glossy layers are used (Sönmez, 1989). A gloss-meter device measuring 60±2 ° was used in the study.

Determination of Color Values

The surface color values of the samples were determined with BYK-Gardner Spectrophotometer colorimeter according to ASTM D2244 standard. Color values were measured according to CIEL*a*b* color coordinate system (Figure 1). This system consisting of three coordinates, L* is in the white-black axis (L* = 0 for black, L* = 100 for white), a* in the red-green axis (positive value is red, negative value is green), and the b* is in the yellow-blue axis (Positive value is yellow, negative value is blue). The total color change/difference (ΔE*) occurring on the sample surfaces after varnishing was determined using Equation 1.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

According to this equation, ΔL* is the difference in the lightness ($L^*_{varnished}$ - $L^*_{control}$), Δa* is the difference in the red-green axis ($a^*_{varnished}$ - $a^*_{control}$), Δb* is the difference in the yellow-blue axis ($b^*_{varnished}$ - $b^*_{control}$). The low value of ΔE* means that the color does not change too much (Söğütlü and Sönmez, 2006). Two measurements were taken on each sample surface and the arithmetic mean was recorded as a single value. Measurements were made perpendicular to the grains.

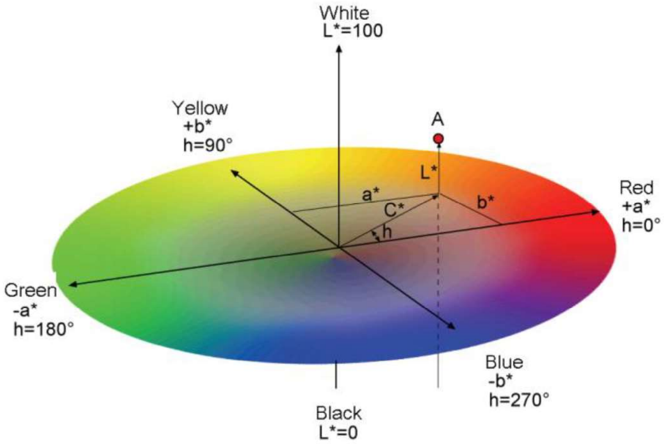

Figure 1: Three Dimensional CIEL*a*b* Color Space (Johansson, 2005)

Statistical Analysis

MSTATC package program was used for statistical evaluations. Variance analysis was applied to determine the effect of NG-added water based varnish on the surface properties of the beech samples at a significance level of 0.05. Also, in the varnished samples, the average values of surface hardness, brightness and color values were compared with Duncan tests.

RESULTS

The results of analysis of variance of surface hardness [perpendicular (⊥) and parallel (//) to grain] and brightness values are given in Table 3. Besides, the variance analysis results of L*, a* and b* color values are shows in Table 4.

Table 3: Results of analysis of variance for hardness and brightness values of samples varnished with water-based varnish modified with NG at different ratios

Factor	Hardness		Brightness (⊥)		Brightness (//)	
	F-value	p≤0.05	F-value	p≤0.05	F-value	p≤0.05
Replication	2.2221	0.0922	0.6879	-	1.6896	0.1831
Varnish type	9.2180	0.0002*	1148.1106	0.0000*	3562.4705	0.0000*

*: Significant at 95% confidence level

Table 3: Results of analysis of variance for L*, a*, b* color values of samples varnished with water-based varnish modified with NG at different ratios

Factor	L*		a*		b*	
	F-value	p≤0.05	F-value	p≤0.05	F-value	p≤0.05
Replication	1.2260	0.3336	2.5979	0.0575	0.5387	-
Varnish type	16176.3044	0.0000*	7823.8282	0.0000*	3086.6802	0.0000*

*: Significant at 95% confidence level

According to the results of variance analysis given in Table 3 and Table 4; the effect of water based varnish applications is significant on the change of surface hardness, brightness and color values of samples ($p \leq 0.05$). The Duncan test results of the average values of hardness and brightness values of the control (unvarnished) and water-based varnish applied samples are given in Table 5.

Table 5: Hardness and brightness value averages of varnished and unvarnished samples

Varnish type	Hardness		Brightness (⊥)		Brightness (//)	
	Mean	*HG*	Mean	*HG*	Mean	*HG*
Unvarnished	51.00	b	2.62	e	3.15	e
WB	57.17	a	67.26	a	85.05	a
WB + 0.25% NG	57.50	a	57.17	b	70.73	b
WB + 0.50% NG	56.83	a	47.67	c	61.18	c
WB + 1% NG	57.00	a	36.26	d	44.17	d
	LSD: 2.672		LSD: 2.170		LSD: 1.557	

HG: Homogeneous Group; LSD: Least Significant Difference; WB: Water Based Varnish; NG: Nano-Graphene

According to Table 5, while the lowest hardness value was obtained in unvarnished samples, the difference between the all varnished samples was found to be statistically insignificant. The surface hardness value of beech samples increased up to 13% after varnishing. The hardness of water-based varnish layer used in the study was found to be higher than the natural hardness of the beech wood. The results are consistent with the literature in this regard (Pelit, 2014). NG, added at different ratios into the water-based varnish, did not change the surface hardness of the varnish samples. In the study, it was predicted that using NG as additive in the water based varnish would increase the hardness values. In the literature, it has been stated that NG has attracted great interest in recent years due to its superior mechanical properties (Dato et al., 2009; Cardinali et al., 2012; Sheshmani and Amini, 2013). However, hardness values are below expected values.

The brightness values of perpendicular (⊥) and parallel (//) to grain were found as lowest for unvarnished samples and highest for varnished ones. With the application of water based varnish, surface brightness value of beech samples increased significantly. However, the surface brightness value of the samples decreased due to the increase NG in the water-based varnish. It was determined that NG showed a matte effect on the varnish layer and reflected light coming to the surface from the light sources back reducing the intensity. In previous studies, it was reported that smooth and perfect surfaces reflect the light coming from a certain direction with a similar or same angle (Sönmez, 1989). Also, on a highly glossy varnish layer, the angle of lights coming to the surface from a light source and reflected from surface are equal (Şanıvar, 2001). In all samples, parallel to grain brightness values were found higher than perpendicular to grain.

The Duncan test results of the average of L*, a* and b* values of the control (unvarnished) and samples coated with water-based varnish are given in Table 6.

Table 6: L*, a*and b* value averages of varnished and unvarnished samples

Varnish type	L*		a*		b*	
	Mean	*HG*	Mean	*HG*	Mean	*HG*
Unvarnished	70.25	a	10.94	b	21.38	b
WB	63.35	b	13.68	a	29.51	a
WB + 0.25% NG	18.78	c	4.25	c	10.65	c
WB + 0.50% NG	6.17	d	1.19	d	2.14	d
WB + 1% NG	4.90	e	-0.11	e	-0.26	e
	LSD: 0.7355		LSD: 0.2015		LSD: 0.6727	

HG: Homogeneous Group; LSD: Least Significant Difference; WB: Water Based Varnish; NG: Nano-Graphene

According to the results of Table 6, the highest L* value was found on unvarnished samples and the lowest L* value was found on samples varnished with % 1 NG added water-based varnish. L* value of all varnished samples is decreased. However, due to the increase in the amount of NG in the water-based varnish, the L* value decreased considerably and the color of the samples is darkened considerably (Figure 2). It has been seen that various matte tones can be obtained in wooden materials with the using of NG in different ratios.

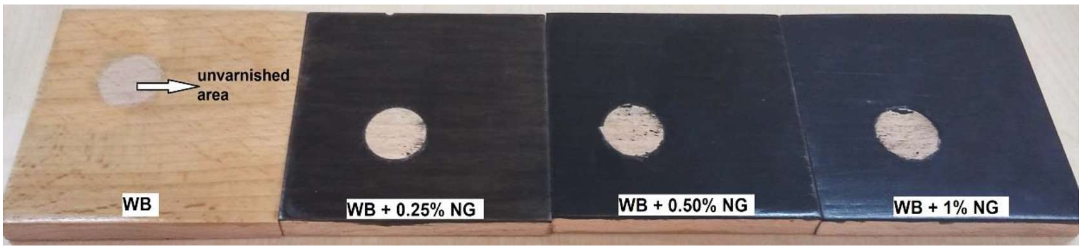

Figure 2: Appearance of samples after varnishing

The highest a* and b* values were found on coated samples varnished with additive-free varnish and the lowest values were found on samples varnished with % 1 NG added water-based varnish. The a* and b* values is increased on varnished samples when compared with unvarnished ones. However, the a* and b* values is decreased on NG added varnish applied samples when compared with control samples. In this case, the red and yellow color values of the samples decreased and the trend of green and blue color increased significantly.

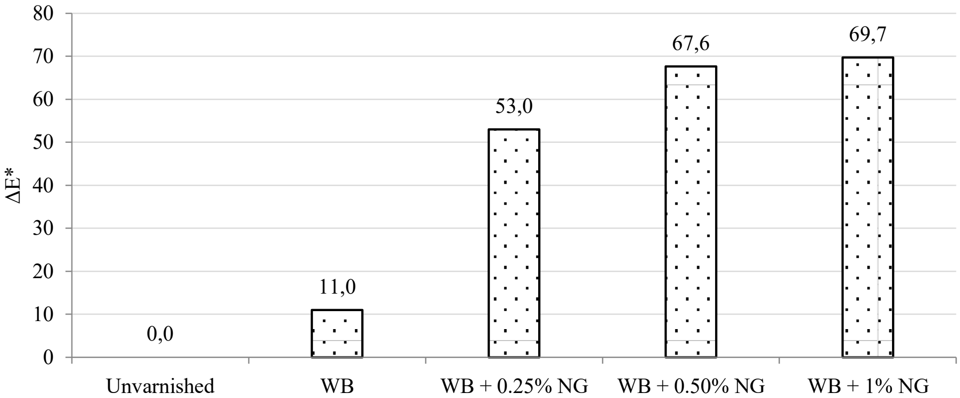

Figure 3: Total Color Change (ΔE*) in Beech Sample after Varnishing with WB

Total color change value calculated with reference to the unvarnished (control) samples is the highest on the samples varnished with 1% NG added varnish (Figure 3). The application of WB varnish changed the value of ΔE* of samples. However, it has been seen that the main factor that affect the value of ΔE* is NG. Due to the increase in NG added to the varnish, the ΔE* value has increased significantly. However, it was found that the ΔE* values of the surfaces varnished with 0.5% and 1% NG added varnish were close to each other.

CONCLUSION

In the study, the hardness, brightness and color values of beech sample surfaces coated with water based varnish modified at different ratios NG were investigated. After varnishing, the surface hardness value of the samples increased up to 13%. However, NG additive has no significant effect on the hardness values, contrary to the predicted. It was determined that the surface brightness values of the samples decreased due to the increase of NG amount on the water-based varnish solution, and NG had an opaque effect on the surfaces. On the other hand, the values of L*, a* and b* decreased significantly with the increase of NG quantity. Samples were greatly darkened and the green-blue color tendency of the samples increased. As a result, it may be recommended that the using of NG in the process of darkening of wood material.

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