Seyyed Khalil Hosseinihashemi[1], Farhad Arwinfar[1], Abdollah Najafi[2],
Ferhat Özdemir[3], Nadir Ayrilmis[4], Abbas Tamjidi[1]

Long-Term Hygroscopic Thickness Swelling Rate of Hydrothermally Treated Beech Wood / Polypropylene Composites

Brzina dugotrajnoga higroskopskog debljinskog bubrenja kompozita od polipropilena i hidrotermički tretirane bukovine

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ABSTRACT • *Long-term hygroscopic thickness swelling rate of polypropylene (PP) composites filled with thermally treated wood flour was investigated. The beech wood chips were heat treated at 120 °C, 150 °C or 180 °C for 30 or 120 min using saturated steam in a digester. The composites based on PP, beech wood flour (BF), and coupling agents (PP-g-MA) were made by melt compounding and injection molding. The weight ratio of BF to PP was controlled at 50/47 for all blends. The amount of coupling agent was fixed at 3 wt.% for all formulations. Further study was conducted to model thickness swelling of the composites, a swelling rate parameter (*K_{SR}*). The thickness swelling of thermally-treated samples at 120 ºC for 30 min and at 150 ºC for 30 min were lower than that of control samples, followed by thermally-treated samples at 180 ºC for 120 min, at 180 ºC for 30 min, at 120 ºC for 120 min, and at 150 ºC for 120 min, respectively. Furthermore, the thickness swelling of the BF/PP composites decreased with increasing time and temperature of the thermal-treatment. In addition, at 120 ºC for 30 min, the composites showed a lower swelling rate than control samples. The *K_{SR}* *of the composites was influenced both by the time and temperature of thermal treatment.*

KEYWORDS: *thickness swelling rate; thermal-treatment; lignocellolusic filler; polypropylene*

SAŽETAK • *U radu je istražen dugotrajni stupanj higroskopskoga debljinskog bubrenja polipropilenskih (PP) kompozita punjenih toplinski obrađenim drvnim brašnom. Iverje od bukovine bilo je toplinski tretirano na 120, 150 ili 180 °C tijekom 30 ili 120 minuta uz pomoć zasićene pare u digestoru. Kompoziti na bazi PP-a, brašna od bukovine (BF)-a i veziva (PP-g-MA) izrađeni su taljenjem i injekcijskim prešanjem. Maseni je omjer BF/PP*

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[1] Author is associate professor, M.Sc. and assistant professor at Department of Wood Science and Paper Technology, Karaj Branch, Islamic Azad University, Karaj, Iran.

[2] Author is associate professor at Department of Wood Science and Paper Technology, Chalous Branch, Islamic Azad University, Chalous, Iran.

[3] Author is assistant professor at Department of Wood Chemistry and Technology, Forestry Faculty, Kahramanmaraş Sütçü İmam University, Oniki Şubat, 46050, Kahramanmaraş, Turkey.

[4] Author is professor at Department of Wood Mechanics and Technology, Forestry Faculty, Istanbul University-Cerrahpasa, Bahcekoy, Sariyer, 34473 Istanbul, Turkey.

za sve smjese bio 50/47. Količina veziva za sve formulacije bila je na 3 wt.%. Nadalje, provedeno je modeliranje debljinskog bubrenja kompozita i parametra brzine bubrenja (KSR). Debljinsko bubrenje uzoraka toplinski tretiranih 30 min na 120 ºC i 30 min na 150 ºC bilo je niže nego na kontrolnim uzorcima, zatim slijede uzorci toplinski tretirani 120 min na 180 ºC, 30 min na 180 ºC, 120 min na 120 ºC, odnosno 120 min na 150 ºC. Nadalje, debljinsko bubrenje BF/PP kompozita smanjivalo se s povećanjem vremena i temperature toplinskog postupka. Osim toga, kompoziti su pri 30 min na 120 ºC pokazali niži parametar brzine bubrenja od kontrolnih uzoraka. Na parametar brzine bubrenja kompozita utjecali su vrijeme toplinskog tretmana i temperatura.

KLJUČNE RIJEČI: *stupanj debljinskog bubrenja; toplinski tretman; lignocelulozno punilo; polipropilen*

1 INTRODUCTION
1. UVOD

Thermal treatment has been used by many researchers to improve dimensional stability of wood and wood-based composites (Kazemi Najafi *et al*., 2007; Kaboorani *et al*., 2008). It decreases the water absorption of wood by the crystallization of cellulose and extraction of hemicelluloses from wood (Wallenberger and Weston, 2004; Yildiz and Gümüşkaya, 2007; Hosseinihashemi *et al*., 2016). The enhancement of the dimensional stability, reduction of the swelling, and alteration of the chemical composition of wood have been found in thermally modified wood (Tjeerdsma *et al*., 2000; Militz and Tjeerdsma, 2001; Yildiz *et al*., 2004; Temiz *et al*., 2006; Rezayati Charani *et al*., 2007; Koubaa *et al*., 2011; Hadi *et al*., 2016).

Under high-temperature conditions, a series of complex chemical reactions takes place in the wood cell wall, such as degradation and condensation reactions (Yin *et al*., 2010). This leads to changes in the amount of the components of wood and also in its physical and chemical properties. After the heat-treatment process, the dimensional stability and the durability of wood increase, which is strongly associated with the reduction in hygroscopicity (Bekhta and Niemz, 2003; Cao *et al*., 2012; Olarescu *et al*., 2014).

Amorphous region of cellulose by heating of wood at high temperature results in an increase in the degree of crystallinity of this polymer. A cross-linkage between the lignin and the polymers occurs because of the thermal degradation of wood, which is responsible for the decrease in the hygroscopicity of wood and the improvement of its dimensional stability (Jämsä and Viitaniemi, 2001; Waskett and Selmes, 2001; Bekhta and Niemz, 2003; Wikberg and Maunu, 2004; Metsä-Kortelainen *et al*., 2006; Calonego *et al*., 2010).

The improvement in the hygroscopic and micromechanical properties of heat-treated wood occurred with an elevation in the steam temperature, which correlated well with this pattern of degradation in the constituents of the biocomposite matrix in the cell wall (Yin *et al*., 2010). Also, the improvement in the dimensional stability of thermally treated wood could be related to a reduction in the number of free hydroxyl groups with chemical reactions (Dale Ellis, 1994; Zhang *et al*., 2006; Deka and Saikia, 2000). This could also be related to the chemical modification in the cell wall of the fiber during the hydrothermal treatment (Yildiz *et al*., 2004; Hadi *et al*., 2016; Rowell and LeVan-Green, 2005). Hemicelluloses degraded by thermal treatment positively affect the dimensional stability of wood (Garrote *et al*., 1999; Tjeerdsma and Militz, 2005). In addition, the reduction of the thickness swelling could be related to the increase of the crystalline regions in the cellulose microfibrils (Wallenberger and Weston, 2004; Yildiz and Gümüşkaya, 2007). Previous studies reported that the swelling loss could occur as a result of esterification of the cellulose microfibrils (Tjeerdsma and Militz, 2005; Boonstra and Tjeerdsma, 2006). In general, the degradation of wood components and particularly of hemicelluloses negatively affects the mechanical properties of wood (Yildiz *et al*., 2006; Korkut *et al*., 2008). Although the effect of heat treatment of wood on thickness swelling of wood plastic composites were investigated by previous studies (Ayrilmis *et al*., 2011; Tufan *et al*., 2016), the long term thickness swelling has not been extensively investigated. In the present study, the effect of thermal-treatment of beech wood on the long-term thickness swelling of the thermoplastic composites was investigated.

2 MATERIALS AND METHODS
2. MATERIJALI I METODE

2.1 Materials
2.1. Materijali

The polymer matrix comprised of V30S polypropylene (PP), with a melt flow index of 16 g/10 min and a density of 0.87 g/cm^3, was supplied by Marun Petrochemical Co. (Mahshahr, Iran). The lignocellulosic material used as the reinforcing filler in the composites was beech (*Fagus orientalis* L.) wood flour, which was ground by a grinder. A maleic anhydride grafted polypropylene (MAPP) as a coupling agent, which was PPG101, was provided by Kimia Javid Sepahan Co. (Tehran, Iran), with a melt flow index of 64 g/10 min, and a density of 0.91 g/cm^3. The amount of the MAPP in all the specimen groups was 3 wt.%.

2.2 Thermal-treatment of wood chips
2.2. Toplinski tretman drvnog iverja

Before the preparation of the composites, beech logs were chipped by a drum-type chipper. Prior to the heat treatment, the wood chips were dried at room temperature for 24 h. After cooling in a desiccator containing silica gel powder, the wood chips were heat treated for 30 or 120 min at different temperatures (120 °C, 150 °C, or 180 °C) using saturated steam in a digester. Then beech wood flour (BWF) was prepared from the treated chips using laboratory type grinder. The wood flour was dried until 0 to 1 % moisture content in an oven at (103±2) °C for 24 h. Polypropylene, beech wood flour, and the coupling agent were then weighed and bagged according to the formulations given in Table 1.

2.3 Preparation and testing of WPCs
2.3. Priprema i ispitivanje WPC-a

The mixing of raw materials was carried out with a counter-rotating intermeshing twin-screw extruder (Model T20, 1990, Dr. Collin GmbH, Germany), with its barrel temperature ranging from 180 °C at six zones, from feeding zone to the die zone, at a screw speed of 60 rpm for 14 min. The pasty compound produced was cooled to room temperature and then grinded to produce suitable granules for further processing. Grinding was carried out in a laboratory mill (Wieser, WGLS 200/200 Model, Germany) and the granulated materials were dried at 105 °C for 4 h. Test specimens were prepared by injection molding machine (Model EM80, Aslanian Co., Iran) set at a temperature ranging from 160 to 180 °C. A complete set of specimens for different tests were produced for each molding operation. Finally, the specimens were conditioned at a temperature of 23 °C and relative humidity of 50 % for at least 40 h, according to ASTM D 618-99 prior to testing. The water absorption (WA) was determined according to ASTM D 570 standard.

2.4 Morphological analysis of WPCs
2.4. Morfološka analiza WPC-a

The morphology of WPCs was characterized using scanning electron microscopy (SEM, Model LEO 440i, Oxford, UK) at 15 kV accelerating voltage. Specimens were first frozen in liquid nitrogen and fractured to ensure that the microstructure remained clean and intact, and then coated with a gold layer to provide electrical conductivity.

2.5 Physical test
2.5. Ispitivanje fizičkih svojstava

Water absorption studies were performed following the ASTM D 570 standard. The water absorption of the WPC specimens with nominal dimensions of 5 mm x 11 mm x 80 mm was determined after 2, 4, 6, 8, 10, 12, 24, 48, 72, 168, 336, 504, 720, and 1440 h immersion in distilled water at room temperature. Three specimens of each type of WPC were dried in an oven for 24 h at (103±2) ºC. The dried specimens were weighed with a precision of 0.001 g and then they were placed in distilled water. At the end of immersion periods, the specimens were removed from the distilled water and the surface water was wiped off using blotting paper. Weight of the specimens was measured at different time intervals during the long-time immersion. The measurements were terminated after the equilibrium weights of the specimens were reached. The values of the water absorption and thickness swelling in percentage were calculated using Eq. 1 and 2:

$$WA\ (t) = [\frac{W(t) - W(o)}{W(o)}] \cdot 100 \tag{1}$$

Where, $WA(t)$ is the water absorption at time t, $W(o)$ is the initial weight of specimens, and $W(t)$ is the weight of specimens at time t (Equation 1).

$$TS\ (t) = [\frac{T(t) - T(o)}{T(o)}] \cdot 100 \tag{2}$$

Where, $TS\ (t)$ is the thickness swelling at time t, $T(o)$ is the initial thickness of specimens, and $T(t)$ is the thickness of specimens at time t (Eq. 2).

Further study was conducted to model long-term thickness swelling behavior of the composites. The swelling rate parameters in the model were obtained by fitting the model predictions with the experimental

Table 1 Composites of the evaluated WPC (wood plastic composite) formulations
Tablica 1. Formulacije istraživanih WPC-ova (drvoplastičnih kompozita)

WPC code *Oznaka WPC-a*	**Treatment type** *Vrsta tretmana*	**Beech wood flour, wt.%** *Drvno brašno od bukovine*, wt.%	**Polypropylene (PP), wt.%** *Polipropilen (PP)*, wt.%	**MAPP^a wt.%**
A	WPC-30 min-120 ºC	50	47	3
B	WPC-30 min-150 ºC	50	47	3
C	WPC-30 min-180 ºC	50	47	3
D	WPC-120 min-120 ºC	50	47	3
E	WPC-120 min-150 ºC	50	47	3
F	WPC-120 min-180 ºC	50	47	3
G	WPC-control	50	47	3

^{a} MAPP – maleic anhydride grafted polypropylene / *polipropilen graftiran anhidridom maleinske kiseline* data. Shi and Gardner (2006) studied to quantify the thickness swelling rate of WPCs for more convenient comparisons. They developed a swelling model describing the hygroscopic swelling process of wood based composites. In this model, a swelling rate parameter (K_{SR}), as determined using the test data, can be used to quantify the swelling rate. The swelling model is described by the following Eq. 3:

$$T(t) = \frac{T_s}{1 + \left(\frac{T_s}{T_o} - 1\right) e^{-K_{SR}\, t}} \tag{3}$$

Where, $T(t)$ is the thickness swelling at time t. T_o and T_s are the initial and equilibrium board thickness, respectively. K_{SR} is a constant referred to as the initial (or intrinsic) relative swelling rate.

The values of K_{SR} in Eq. 3 depend on how fast the composites swell and also on their equilibrium thickness swelling. Non-linear curve fitting was used to find the swelling rate parameter (K_{SR}) that provided the best fit between the equation and the experimental data. This algorithm seeks the parameter values that minimize the sum of the squared differences between the observed and predicted values of the dependent variable as seen in Eq. 4,

$$ss = \sum_{i=1}^{n} \left(y_i - \overline{y_i}\right)^2 \tag{4}$$

Where, SS is the sum of squared difference and y_i, and $\bar{y}_i$ are the observed and predicted values of the dependent variable, respectively.

2.6 FT-IR analysis
2.6. FT-IR analiza

FT-IR measurements were carried out in an Equinox instrument (Bruket Co., Germany) by direct transmittance using KBr pellet technique. Each spectrum was recorded at a rate of 10 scans, in the range from 3500 to 800 cm^{-1} with a resolution of 4 cm^{-1}.

3 RESULTS AND DISCUSSION
3. REZULTATI I RASPRAVA

3.1 Long term water absorption and thickness swelling behavior
3.1. Dugotrajno upijanje vode i debljinsko bubrenje

Long-term water absorption and thickness swelling of the composites after 1440 h immersed in water are presented in Figures 1 and 2. Generally, water absorption and thickness swelling increased with immersion time, reaching a certain value beyond which weight and thickness increased no more. At the early stage of the water uptake test, as compared with the long term test, the composites clearly absorbed more water as well as faster. The composites containing thermally treated beech wood flour had longer equilibrium time (time to reach the equilibrium water absorption and thickness swelling) (Figures 1 and 2). Furthermore, the composites containing thermally treated beech wood flour swelled and gained weight very slowly.

The independent effects of thermal-treatment temperatures and durations on the long-term thickness swelling of WPCs are presented in Figures 3 and 4. A significant correlation was found between the treatment time and long term thickness swelling. A similar relationship was determined for the treatment temperature.

Exposure duration and temperature are two important factors affecting hemicelluloses degradation (Ayrilmis *et al.* 2011; Militz and Tjeerdsma, 2001). Cumulative thermal exposure in the hot-press alters the hemicelluloses structure because arabinan and galactan, each a side-chain component of the hemicelluloses, tend to be more degraded as the chip size decrease (Winandy and Krzysik, 2007). These changes in the chemistry of hemicelluloses seem to reduce the hygroscopicity of the flakes. A lower internal void vol-

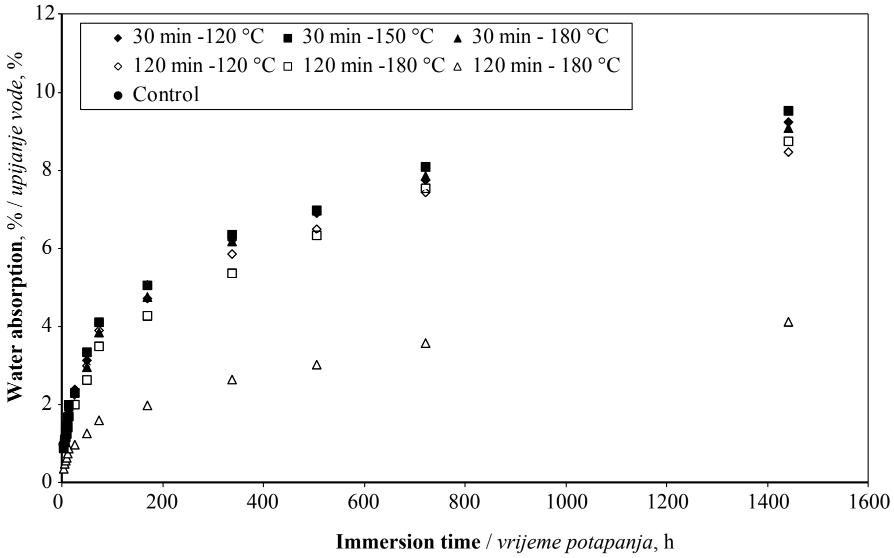


Figure 1 Effect of thermal-treatment severity on long-term water absorption of WPCs
Slika 1. Utjecaj jačine toplinskog tretmana na dugotrajno upijanje vode WPC-a

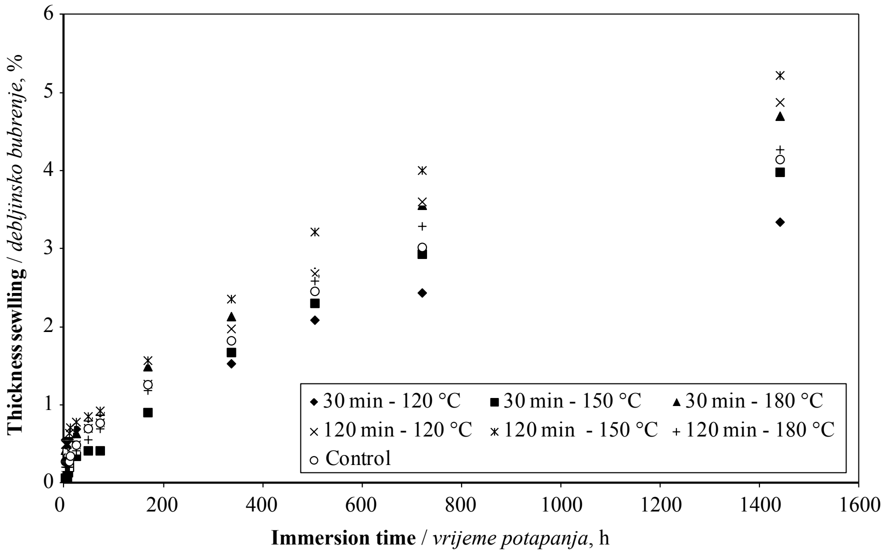


Figure 2 Effect of thermal-treatment severity on long-term thickness swelling of WPCs
Slika 2. Utjecaj jačine toplinskog tretmana na dugotrajno debljinsko bubrenje WPC-a

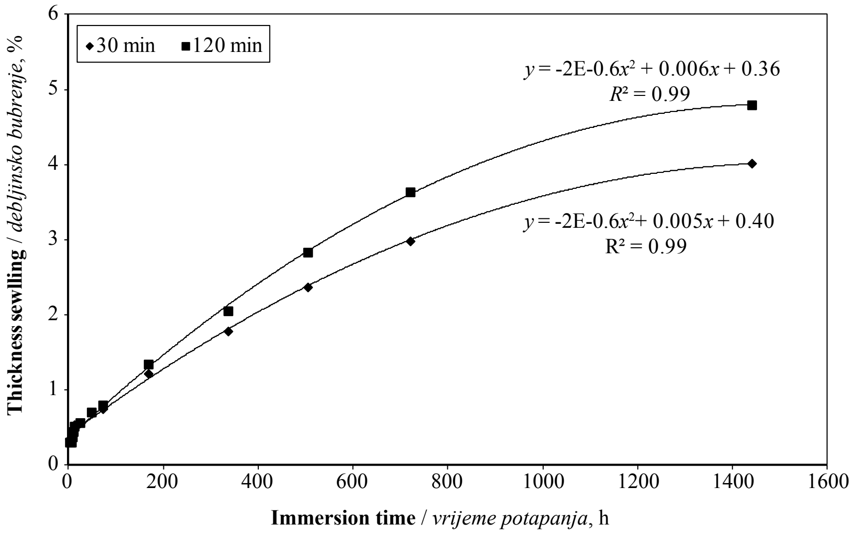


Figure 3 Independent effect of thermal-treatment times on long-term thickness swelling of WPCs
Slika 3. Neovisni učinak trajanja toplinskog tretmana na dugotrajno debljinsko bubrenje WPC-a

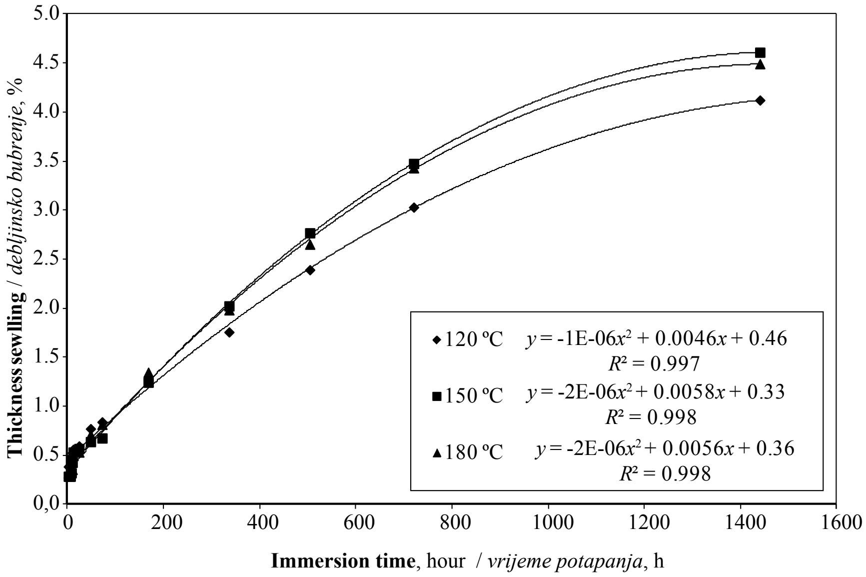


Figure 4 Independent effect of thermal-treatment temperatures on long-term thickness swelling of WPCs
Slika 4. Neovisni učinak temperature toplinskog tretmana na dugotrajno debljinsko bubrenje WPC-a

Table 2 Swelling rate parameters for studied composites
Tablica 2. Parametri brzine bubrenja istraživanih kompozita

WPC code *Oznaka WPC-a*	**Maximum thickness swelling, %** *Najveće debljinsko bubrenje, %*	**Maximum value of K_{sr}× 10^{-3}, h^{-1}** *Najveća vrijednost K_{sr}× 10^{-3}, h^{-1}*	**Sum of squared** *Zbroj kvadrata*
A	3.35	0.0023	2.51
B	3.99	0.0018	0.27
C	4.70	0.0021	1.74
D	4.88	0.0019	0.99
E	5.23	0.0021	2.08
F	4.27	0.0021	0.44
G	4.15	0.0020	0.73

ume might obstruct the migration of moisture and diminish the convective effect. The decrease of hemicellulose content results in a decrease of hydroxyl groups, which also include free hydroxyl groups, thus decreasing the water absorption capacity of wood. Water absorption of untreated wood was the greatest. The greater water uptake of samples with greater weight loss could be due to the possible presence of larger and more numerous pores in these samples, resulting in increased capillary action of water.

The swelling rate parameter (K_{SR}) and maximum values of thickness swelling of the composites are given in Table 2.

The composites produced by a 120 min / 150 °C treatment had the highest thickness swelling. The minimum K_{SR} was calculated for the composites produced with beech wood flour treated at 120 °C for 30 min. The maximum value of K_{SR} was found in the composites produced with wood flour at 150 °C for 30 min. It is important to note that in the swelling model K_{SR} was obtained considering the whole thickness process until it was equilibrated. It is dependent not only on the initial rate of swelling but also on the equilibrium thickness swelling of the composites (Shi and Gardner, 2006; Kord, 2013). Less time was required to reach the equilibrium thickness for thermally treated beech wood flour/PP composites (Figure 2). This can be explained by very high K_{SR} value determined in the wood flour filled composites. The correlation between predicted and experimental thickness swelling is given in Table 3.

Table 3 Correlation between predicted and experimental thickness swelling
Tablica 3. Korelacija između predviđenoga i eksperimentalnoga debljinskog bubrenja

WPC code / *Oznaka WPC-a*	R^{2*}
A	0.98
B	0.99
C	0.99
D	0.99
E	0.99
F	1.00
G	0.99

* R – squared / *R – kvadrat*

Table 4 Relationship between long-term water absorption (*WA*) and thickness swelling (*TS*) in studied composites
Tablica 4. Odnos između dugotrajnog upijanja vode (*WA*) i debljinskog bubrenja (*TS*) ispitivanih kompozita

WPC code *Oznaka WPC-a*	**Equation** *Jednadžba*	R^{2*}
A	$TS= 0.30\ WA + 0.02$	0.92
B	$TS= 0.42\ WA – 0.63$	0.92
C	$TS= 0.47\ WA – 0.32$	0.93
D	$TS= 0.53\ WA – 0.56$	0.90
E	$TS= 0.57\ WA – 0.34$	0.95
F	$TS= 1.05\ WA – 0.56$	0.96
G	$TS= 0.46\ WA – 0.25$	0.98

* R – squared / *R – kvadrat*

Figures 5 and 6 indicate fitting predicted thickness swelling with the experimental data obtained from thermally treated beech wood flour/PP composites for calculating the swelling rate.

The relationship between long-term water absorption and thickness swelling in the composites is given in Table 4. Thickness swelling is a response to absorbed water in the composites. The R-squared values of all the composites were found to be 0.90 (Table 4).

3.2 FT-IR analysis
3.2. FT-IR analiza

FT-IR spectroscopy is a simple technique applied to determine the effect of various applications used in order to obtain information about the structure of wood components causing changes in the chemical structure of wood. It is preferred because it needs only a small sample size and short analysis time for test application, as well as because it does not disrupt wood structure. Due to their complex nature, spectra are considered as two regions for examination. The first region is expressed as 2700-4000 cm^{-1} band where the OH and C-H stretching vibrations are included, while the second region is defined as the “Fingerprint” region between at 1100-1800 cm^{-1} where different vibration extension regions of wood components are identified.

Band assignment of wood material in the 4000-800 cm^{-1} region is presented in Table 5 (Li *et al.*, 2015). FT-IR spectroscopy of the test specimens treated at 120

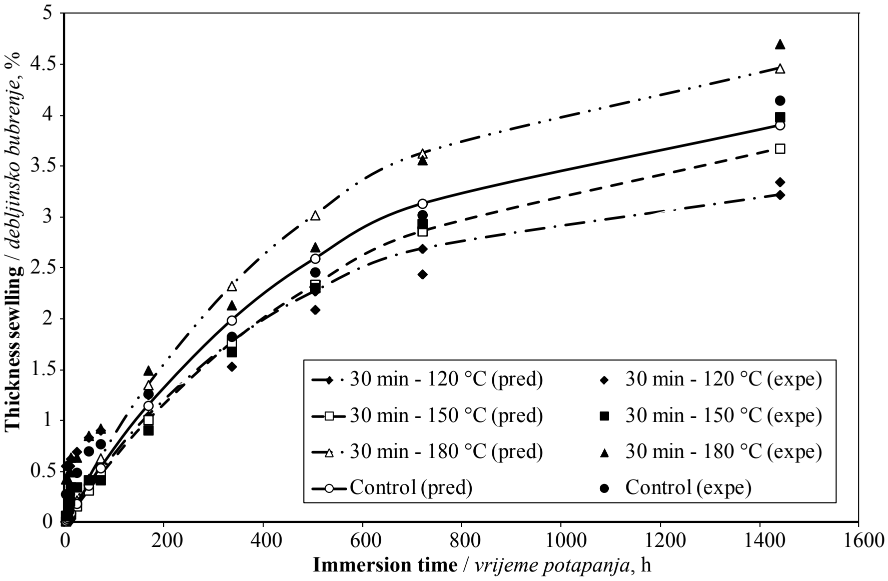


Figure 5 Fitting predicted thickness swelling with experimental data for WPC specimens produced with thermally treated wood particles at different temperatures for 30 min
Slika 5. Uparivanje predviđenoga debljinskog bubrenja s eksperimentalnim podatcima za WPC uzorke proizvedene s toplinski tretiranim drvnim **česticama** 30 min na različitim temperaturama

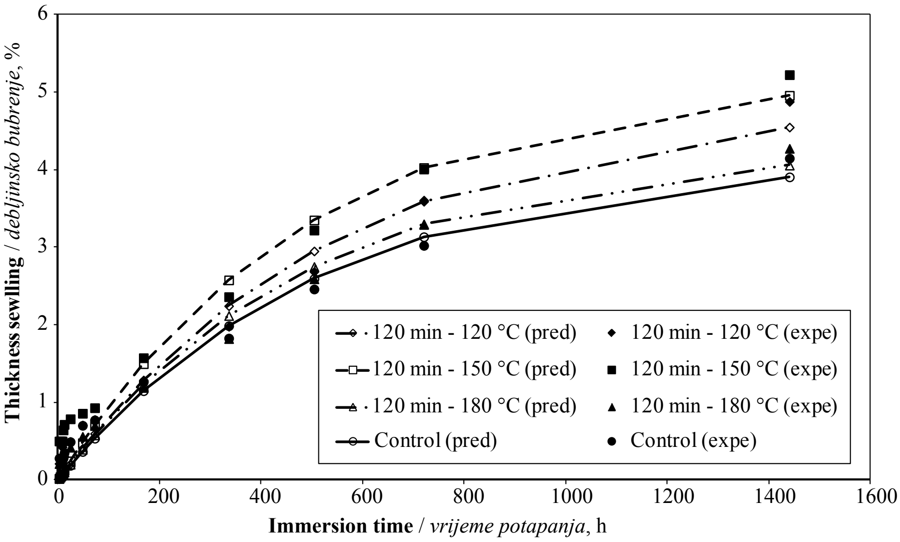


Figure 6 Fitting predicted thickness swelling with experimental data for WPC specimens produced with thermally treated wood particles at different temperatures for 120 min
Slika 6. Uparivanje predviđenoga debljinskog bubrenja s eksperimentalnim podatcima za WPC uzorke proizvedene s toplinski tretiranim drvnim **česticama** 120 min na različitim temperaturama

°C and 180 °C with control samples was recorded. As shown in Figure 7, the peak intensity of the OH stretches at about 3400 cm^{-1} in test specimens exposed to temperatures of 180 °C and 120 °C reduced as compared to the control sample. The C-H deformations in lignin and carbohydrates were observed around 1462 cm^{-1}. When the exposure time of the test specimens at 180 °C increased, aromatic and aliphatic C-H (methylene groups) stretches were determined between 2800 and 2920 cm-^{1}. Similarly, the C=O carboxyl groups were observed between 1731 and 1737 cm-^{1}. In 1596 cm^{-1} C=C aromatic skeletal vibration (lignin) peak value, peak intensity showed an increase due to the temperature increase. The intensity of the C-O stretching peak of lignin at 1250 cm^{-1} decreased with the effect of temperature. The C-O stretching vibration in cellulose and hemicelluloses formed at 1054 cm^{-1} was slightly degraded. The cellulose and hemicellulose C-H deformations and C-O-C stretches formed at 1377 cm^{-1} and 1169 cm^{-1}, respectively.

As a result, the IR peaks were not affected by the heat treatment temperature. However, the intensities of the functional groups, in particular for –OH stretches, decreased at 180 °C as compared to the control samples at lower temperature (150 °C and 180 °C). Thus, it can be said that some functional groups such as –OH or

Table 5 Band assignment of wood samples in 4000-800 cm^{-1} region (Li *et al*., 2015)
Tablica 5. Vrpce pripisane uzorcima drva u području 4000 – 800 cm^{-1} (Li *et al*., 2015.)

Wavenumber, cm^{-1} *Valni broj,* cm^{-1}	**Band assignment** *Pripisane vrpce*
3399	O-H stretching in hydroxyl groups
2921	C-H asymmetric stretching in methylene groups
1736	C=O stretching vibration of carbonyl, carboxyl and acetyl groups
1659	Conjugated C-O in quinines coupled with C=O stretching of various groups
1594	C=C stretching of aromatic skeletal in lignin
1508	C=C stretching of aromatic skeletal in lignin
1463	C-H deformation in lignin and carbohydrates
1423	C-H deformation in lignin and carbohydrates
1374	C-H deformation in cellulose and hemicellulose
1328	C-H vibration in cellulose and C-O vibration in syringyl derivatives-condensed structures in lignin
1266	C-O stretching in lignin
1234	C-O stretching vibration of Ph-O-C coupled with aromatic ring vibration in lignin and C-O stretching vibration in xyloglucan
1157	C-O-C stretching vibration in cellulose and hemicelluloses
1055	C-O stretching vibrations in cellulose and hemicelluloses
1034	C-O ester stretching vibrations in methoxyl and β-O-4 linkages in lignin
897	Character of cellulose P-chains, C-H stretching out of plane of aromatic ring

carboxylic acid C=O groups reacted with each other at 180 °C and formed new ester or etheric groups in addition to –OH or C=O stretches.

3.3 Morphological analysis
3.3. Morfološka analiza

The morphological analysis of the composites is presented in Figure 8. The SEM images revealed that there was some distortion and modification of the cell walls of wood due to the hydro-thermal treatment. The cracks in the cell walls of wood increased with increasing the treatment temperature and time. The melted PP polymer filled the cracks in the cell walls of wood based on the SEM images, thus decreasing the thickness swelling.

4 CONCLUSIONS
4. ZAKLJUČAK

The composites produced with thermally treated beech wood flour swelled and gained weight very slowly. The thickness swelling of the composites decreased with increasing time and temperature of the thermal-treatment. In addition, at 120 ºC for 30 min, the composites showed a lower swelling rate than control samples. The K_{SR} of the composites was influenced by both the time of thermal treatment and temperature. A strong correlation was found between the long-term water absorption and thickness swelling in the composites. Based on the findings obtained from the present study, it can be said that thermal treatment of the

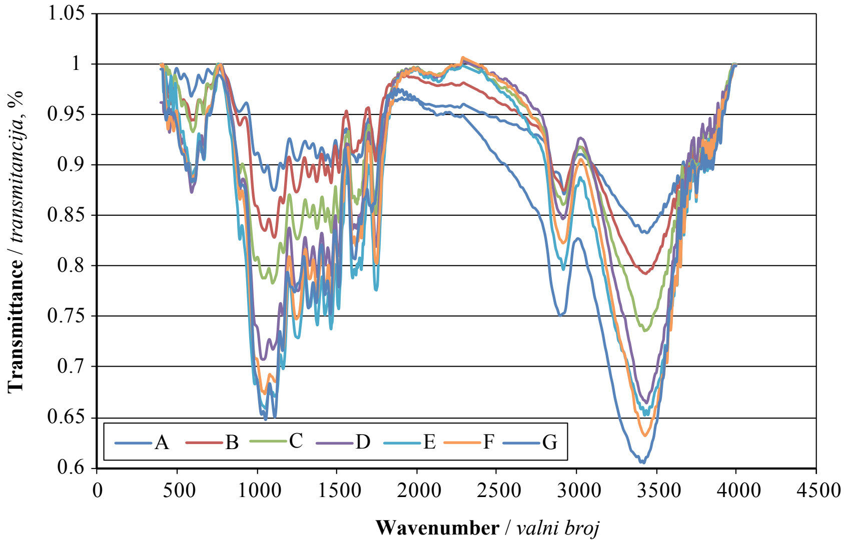
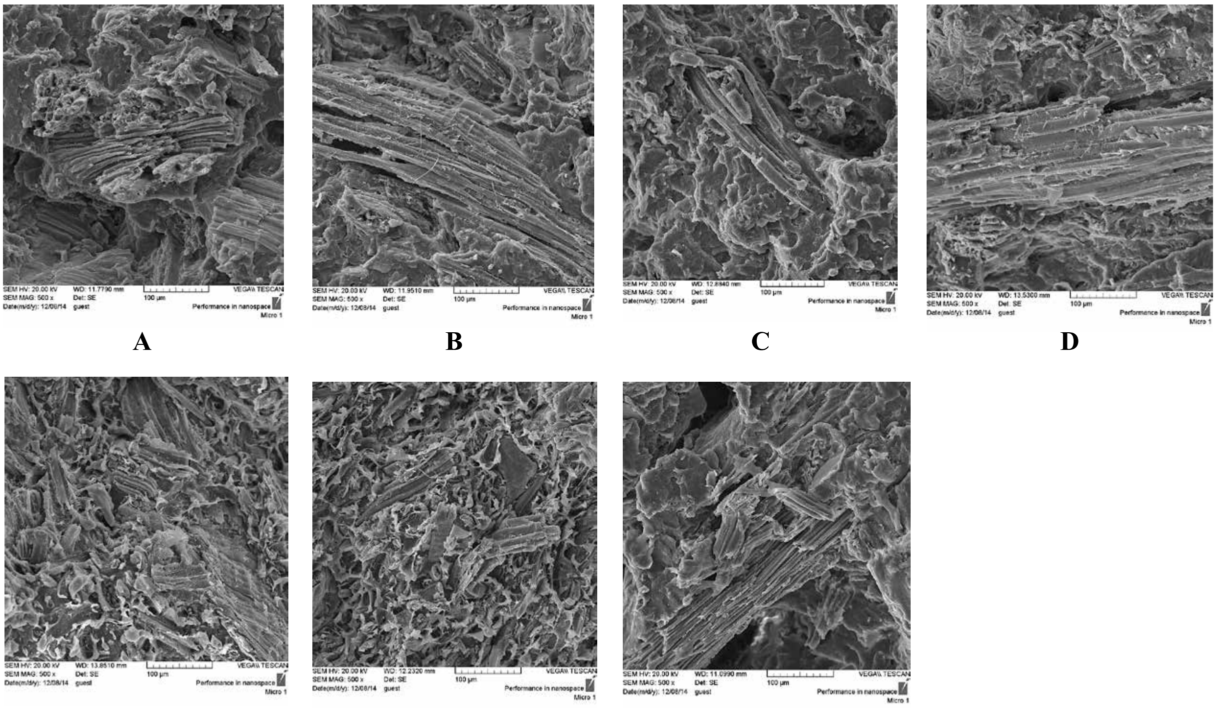


Figure 7 FT-IR spectrum of heat treated and untreated test samples (A, B, C, D, E, F and G according to Table 2)
Slika 7. FT-IR spektri toplinski tretiranih i netretiranih uzoraka (A, B, C, D, E, F i G prema tablici 2.)


A B C D

E F G

Figure 8 SEM micrograph of fracture surfaces in WPC specimens produced with thermally treated wood particles at different times and temperatures (A, B, C, D, E, F, and G according to Table 2)
Slika 8. SEM mikrografije lomnih površina u WPC uzorcima proizvedenim s toplinski tretiranim drvnim česticama pri različitom vremenu i temperaturi tretiranja (A, B, C, D, E, F i G prema tablici 2.)

wood chips at 150 °C for 30 min result in optimal parameters for the wood flour reinforced polypropylene composites, as they have higher water resistance than other treatment groups.

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5 REFERENCES
5. LITERATURA

1. Ayrilmis, N.; Jarusombuti, S.; Fueangvivat, V.; Bauchongkol, P., 2011: Effect of thermal-treatment of wood fibres on properties of flat-pressed wood plastic composites. Polym Degradation and Stability, 96 (5): 818-822. https://doi.org/10.1016/j.polymdegradstab.2011.02.005
2. Bekhta, P.; Niemz, P., 2003: Effect of high temperature on the change in color, dimensional stability and mechanical properties of spruce wood. Holzforschung, 57 (5): 539-546. https://doi.org/10.1515/HF.2003.080
3. Birinci, E.; Kaymakci, A.; Dundar, T.; Ayrilmis, N., 2016: Effect of heat-treatment on some properties of wood plastic composites. Proceeding of International Forestry Symposium, Kastamonu, Turkey.
4. Boonstra, M. J.; Tjeerdsma, B., 2006: Chemical analysis of heat treated softwoods. Holz als Roh- und Werkstoff, 64: 204-211. https://doi.org/ 10.1007/s00107-005-0078-4
5. Calonego, F. W.; Severo, E. T. D.; Furtado, E. L., 2010: Decay resistance of thermally modified *Eucalyptus grandis* wood at 140 °C, 160 °C, 180 °C, 200 °C, and 220 °C. Bioresource Technology, 101 (23): 9391-9394. https://doi.org/10.1016/j.biortech.2010.06.119
6. Cao, Y.; Lu, J.; Huang, R.; Jiang, J., 2012: Increased dimensional stability of Chinese fir through steam-heat treatment. European Journal of Wood and Wood Products, 70 (4): 441-444. http://doi.org/10.1007/s00107-011-0570-y
7. Deka, M.; Saikia, C. N., 2000: Chemical modification of wood with thermosetting resin: Effect on dimensional stability and strength property. Bioresource Technology, 73 (2): 179-181. https://doi.org/ 10.1016/S0960-8524(99)00167-4
8. Dale Ellis, W., 1994: Moisture sorption and swelling of wood-polymer composites. Wood and Fiber Science, 26 (3): 333-341.
9. Garrote, G.; Dominiguez, H.; Parajó, J. C., 1999: Hydrothermal processing of lignocellulosic materials. Holz als Roh- und Werkstoff, 57 (3): 191-202. https://doi.org/10.1007/s001070050039
10. Hadi, S.; Hosseinihashemi, S. K.; Jahan Latibari, A.; Salem, M. Z. M., 2016: Effects of acid copper chromate preservative and hydrothermal treatment on the dimensional stability, hardness, and decay resistance of poplar wood. BioResources, 11 (2): 4850-4864. https://doi.org/10.15376/biores.11.2.4850-4864
11. Hosseinihashemi, S. K.; Arwinfar, F.; Najafi, A.; Nemli, G.; Ayrilmis, N., 2016: Long-term water absorption behavior of thermoplastic composites produced with thermally treated wood. Measurement, 86: 202-208. https://doi.org/10.1016/j.measurement.2016.02.058
12. Jämsä, S.; Viitaniemi, P., 2001: Heat treatment of wood: Better durability without chemicals. Special Seminar: Environmental Optimization of Wood Protection. In: Proceedings of special seminar held in Antibes, France, pp. 68.

13. Kaboorani, A.; Faezipour, M.; Ebrahimi, G. H., 2008: Feasibility of using heat treated wood in wood thermoplastic. Journal of Reinforced Plastics and Composites, 27 (16-17): 1689-1699. https://doi.org/ 10.1177/0731684407084207
14. Kazemi Najafi, S.; Kiaefar, A.; Tajvidi, M.; Hamidina, E., 2007: Water absorption behavior of composites from sawdust and recycled plastics. Journal of Reinforced Plastics and Composites, 26 (3): 341-348. https://doi.org/10.1177/0731684407072519
15. Kord, B., 2013: Natural durability of organomodified layered silicate filled wood flour reinforced polypropylene nanocomposites. Science and Engineering of Composite Materials, 20 (3): 227-232. https://doi.org/10.1515/secm-2012-0092
16. Korkut, S.; Akgül, M.; Dündar, T., 2008: The effects of heat treatment on technological properties of Scots pine (*Pinus sylvestris* L.) wood. Bioresource Technology, 99 (6): 1861-1868. https://doi.org/ 10.1016/j.biortech.2007.03.038
17. Koubaa, A.; Ding, W. D.; Chaala, A.; Bouafif, H., 2011: Surface properties of methyl methacrylate hardened hybrid poplar wood. Journal of Applied Polymer Science, 123 (3): 1428-1436. https://doi.org/ 10.1002/app.33799
18. Li, M. Y.; Cheng, S. C.; Li, D.; Wang, S. N.; Huang, A. M.; Sun, S. Q., 2015: Structural characterization of steam-heat treated *Tectona grandis* wood analyzed by FT-IR and 2D-IR correlation spectroscopy. Chinese Chemical Letters, 26 (2): 221-225. http://doi.org/10.1016/j.cclet.2014.11.024
19. Metsä-Kortelainen, S.; Anitikainen, T.; Viitaniemi, P., 2006: The water absorption of sapwood and heartwood of Scots pines and Norway spruce heat-treated at 170 °C, 190 °C, 210 °C and 230 °C. Holz als Roh- und Werkstoff, 64 (3): 192-197. http://doi.org/ 10.1007/s00107-005-0063-y
20. Militz, H.; Tjeerdsma, B., 2001: Heat treatment of wood by the PLATO-Process. In: Review on Heat Treatments Wood. Cost Action E 22, Proceeding of Special Seminar, Antibes, France.
21. Olarescu, M. C.; Campean, M.; Ispas, M.; Cosereanu, C., 2014: Effect of thermal treatment on some properties of lime wood. European Journal of Wood and Wood Products, 72 (4): 559-562. http://doi.org/10.1007/s00107-014-0809-5
22. Rezayati Charani, P.; Rovshandeh, J. M.; Mohebby, B.; Ramezani, O., 2007: Influence of hydrothermal treatment on the dimensional stability of beech wood. Caspian Journal of Environmental Sciences, 5 (2): 125-131.
23. Rowell, R. M.; LeVan-Green, S., 2005: Thermal properties. In: Handbook of Wood Chemistry and Wood Composites, Rowell, R. M. (ed.), CRC Press, Boca Raton, FL.
24. Schaudy, R.; Proksch, E., 1982: Wood-plastic combinations with high dimensional stability. Industrial and Engineering Chemistry Product Research and Development, 21 (3): 369-375. https://doi.org/ 10.1021/i300007a006
25. Shi, S. Q.; Gardner, D. J., 2006: Hygroscopic thickness swelling rate of compression molded wood fiberboard and wood fiber/polymer composites. Composites, Part A: Applied Science and Manufacturing, 37 (9): 1276-1285. https://doi.org/10.1016/j.compositesa.2005.08.015
26. Temiz, A.; Yıldız, U. C.; Nilsson, T., 2006: Comparison of copper emission rates from wood treated with different preservatives to the environment. Building and Environment, 41 (7): 910-914. https://doi.org/10.1016/j.buildenv.2005.04.001
27. Tjeerdsma, B. F.; Stevens, M.; Militz, H., 2000: Durability aspects of hydrothermal treated wood. International Research Group on Wood Preservation, Section 4 – Processes, IRG/WP 00-40160.
28. Tjeerdsma, B. F.; Militz, H., 2005: Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. Holz als Roh- und Werkstoff, 63 (2): 102-111. https://doi.org/ 10.1007/s00107-004-0532-8
29. Tufan, M.; Gulec, T.; Pesman, E.; Ayrilmis, N., 2016: Technological and thermal properties of thermoplastic composites filled with heat-treated alder wood. BioResources, 11 (2): 3153-3164. https://10.15376/biores.11.2.3153-3164
30. Wallenberger, F. T.; Weston, N., 2004: Natural Fibers, Plastic and Composites, Springer, New York, NY.
31. Waskett, P.; Selmes, R. E., 2001: Opportunities for UK grown timber: Wood modification state of the art review. Project Report Number 203-343, Building Research Establishment, Watford, UK.
32. Wikberg, H.; Maunu, S. L., 2004: Characterization of thermally modified hard-and softwoods by 13C CPMAS NMR. Carbohydrate Polymers, 58 (4): 461-466. https://doi.org/10.1016/j.carbpol.2004.08.008
33. Winandy, J. E.; Krzysik, A., 2007: Thermal degradation of wood fibers during hot-pressing of MDF composites, Part I. Relative effects and benefits of thermal exposure. Wood and Fiber Science, 39 (3): 450-461.
34. Yildiz, U.; Gercek, Z.; Gezer, E.; Serdar, B.; Yildiz, S.; Gezer, E. D.; Dizman, E.; Temiz, A., 2004: The effects of heat treatment on anatomical changes of beech wood, IRG WP02- 40223.
35. Yildiz, S.; Gezer, E. D.; Yildiz, Ü. C., 2006: Mechanical and chemical behavior of spruce wood modified by heat. Building and Environment, 41 (12): 1762-1766. https://doi.org/10.1016/j.buildenv.2005.07.017
36. Yildiz, S.; Gümüşkaya, E., 2007: The effects of thermal modification on crystalline structure of cellulose in soft and hardwood. Building and Environment, 42 (1): 62-67. https://doi.org/10.1016/j.buildenv.2005.07.009
37. Yin, Y.; Berglund, L.; Salmén, L., 2010: Effect of steam treatment on the properties of wood cell walls. Biomacromolecules, 12 (1): 194-202. http://doi.org/10.1021/bm101144m
38. Zhang, Y.; Zhang, S. Y.; Yang, D. Q.; Wan, H., 2006: Dimensional stability of wood-polymer composites. Journal of Applied Polymer Science, 102 (6): 5085-5094. https://doi.org/ 10.1002/app.23581

Corresponding address:

Assoc. Prof. SEYYED KHALIL HOSSEINIHASHEMI

Department of Wood Science and Paper Technology, Karaj Branch, Islamic Azad University, Karaj, Iran.
e-mail: hashemi@kiau.ac.ir