

Thermally initiated solvent-free radical modification of beech (*Fagus sylvatica*) wood

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Abstract A procedure for rapidly modifying beech wood using a thermally initiated solvent-free grafting system was examined. In the modification, butyl acrylate and butyl methacrylate were used as vinyl monomers. Free radicals were generated from 2,2'-azobis(2-methylpropionitrile) or benzoyl peroxide at 103 and 180 °C by contact heating of the modified material. Chemical changes in the material were investigated by FTIR and X-ray photoelectron spectroscopies. The modification resulted in decreased surface wetting of the material manifested by increased water contact angles. The hardness of the resultant material decreased, while its color changed by the effect of temperature. It was shown that the approach allowed for efficient thermal-initiated modification of wood with rapid contact heating.

Introduction

The modification of wood is not a new idea, since alternations in wood properties provide many advantages of the resultant product over the unmodified materials:

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improved photostability (Chang and Chang 2001), reduced water sorption, dimensional stability, susceptibility to bioattack (Hill et al. 2005; Gabrielli and Kamke 2010) and—last but not least—higher resistance to the weather (Evans et al. 2002). The chemical and impregnation modifications of wood were already reported in the 1940s (Stamm and Seborg 1936; Stamm and Trakow 1947). Since that time, numerous reports on wood modification have been published. There are three general approaches to wood modification: (1) lumen filling, (2) bulking treatments, and (3) grafting with covalent bond formation (Homan and Jorissen 2004). The chemical grafting of wood usually requires a solvent environment and numerous types of reagents and processes such as (1) urethanes using isocyanate-alcohol monoadducts (Engonga et al. 2000), (2) alkylation using alkyl chlorides (Prakash and Mahadevan 2008; Dominkovics et al. 2007; McDonald and Ma 2010), and (3) esterification using vinyl esters (Jebrane and Sébe 2008). Unfortunately, there are some limitations to these procedures notably cost, energy demand from solvent evaporation, and environmental impacts that can impede their industrial applications.

As an alternative to chemical approaches, the physical treatments (e.g., thermal treatment, UV or plasma treatment) may be considered (Jamali and Evans 2011). They are easy, rapid, safe and require no solvent, so that the thermal treatments have already been commercialized (e.g., ThermoWood[®] by Finnish ThermoWood Association or Retification[®] by Retitech).

There are many papers regarding grafting of synthetic vinyl monomers like styrene, acrylamide, acrylonitrile onto lignin or hemicellulose by free radical copolymerization in chemical initiation of radicals (Phillips et al. 1972; Fanta et al. 1982; Meister et al. 1984, 1991; Meister and Patil 1985; Meister and Chen 1993) or chemoenzymatical (Milstein et al. 1989; Milstein et al. 1993, 1994; Mai et al. 2000). There are also reports on free radicals generation using high-frequency ultrasound (Petrier et al. 1994; Gadhe et al. 2006), UV laser energy (Dodson et al. 2009), or γ -irradiation (Supe et al. 1993) which, in fact, are a combination of physical and chemical modification. Moreover, many successful radical graftings were efficiently applied to a range of lignocellulosic materials—like high-yield pulp (Hornof et al. 1976), wheat straw (Fanta et al. 1987), or jute fiber (Huque et al. 1980; Abou-Zeid et al. 1984; Sikdar et al. 1995). However, the procedures were performed in solvents, which undoubtedly are a serious inconvenience limiting scaling up.

Thus, in order to overcome that disadvantage and perform a chemical modification in a solvent-free system, a rapid procedure based on thermally initiated radical grafting with contact heating was examined in this paper. The approach seems to be a feasible and efficient. Butyl acrylate and butyl methacrylate are used as monomers. It was expected that water repellency effect of alkyl chains covalently bonded to the substrate would be a guide to the alternation in material interactions with water. Therefore, surface wetting was investigated by observation of the contact angle, while chemical changes in wood structure were observed by FTIR and XPS spectroscopy.

Materials and methods

Monomers: butyl acrylate (BA) and butyl methacrylate (BM) as well as radical initiators 2,2'-azobis(2-methylpropionitrile) (AIBN) and benzoyl peroxide (BP) were used as purchased from Sigma-Aldrich.

Peeled beech (*Fagus sylvatica* L.) veneers of dimensions $50 \times 30 \times 2 \text{ mm}^3$ or solid beech specimens of dimensions $30 \times 50 \times 10 \text{ mm}^3$ (radial \times tangential \times longitudinal) were—prior to modification—Soxhlet extracted with toluene–acetone (4:1, v/v) for 4 h and then dried overnight at $103 \text{ }^\circ\text{C}$. The specimens were soaked with 1 % solution of an initiator in the respective monomer and subjected to contact heating with hot platens to $103 \text{ }^\circ\text{C}$ for 30 min or to $180 \text{ }^\circ\text{C}$ for 10 min. After the modification, the specimens were re-extracted to remove excess reagents and dried overnight. Same extraction, drying and surface heating procedures were applied to the controls.

Water contact angle

The sessile droplet method was used for the contact angle measurements. A Phoenix 300 contact angle analyzer (SEO, Korea) equipped with microscopic lenses and CCD camera was used. The average contact angles as well as spreading curves are means of 15 measurements.

FTIR spectroscopy

Spectra of wood material were collected in KBr discs using a Bio-Rad FTS 165 FTIR spectrometer. Each spectrum was taken as an average of 32 scans at a resolution of 4 cm^{-1} .

Color measurements

Due to the surface heating, both the vinyl monomer-modified and unmodified specimens (controls) were subjects of color change. In order to determine the effect of temperature on the color of controls, raw untreated specimens were used as zero references in calculations. The color of the samples was described using the CIE $L^*a^*b^*$ coordinates using an SP-60 (X-Rite) spectrophotometer. Total color changes ΔE were determined according to EN 7224-3:2003 using the Euclidean distance Eq. (1):

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

where ΔE total color change, ΔL sample lightening/darkening, Δa red/green shift, Δb yellow/blue shift.

Hardness

Hardness of the modified solid beech was determined using a Brinell digital hardness tester CV-3000LDB (Bowers Metrology, UK) and calculated according to EN ISO 6506-1 2008 standard using the following formula (2):

$$HB = \frac{2P}{\pi D[D - \sqrt{D^2 - d^2}]} \quad (2)$$

where P loading (kG), D ball diameter 10 mm, and d indentation diameter [mm].

Scanning electron microscopy (SEM)

The SEM images were made using Quanta 200 ESEM (FEI) instrument, pressure 1.0 Torr, applied voltage 25 kV. Prior to analysis, the specimens were gold coated.

X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed on a limited number of samples on both control and treated samples to determine surface chemical composition. A custom built spectrometer using two monochromators at 1,253 and 1,487 eV with a resolution of 50 meV was employed. Charging was minimized using a flood gun. Samples were mounted on a stainless steel sample holder with carbon tape. Two types of spectra were obtained that include low-resolution spectra from 0 to 1,100 eV binding energy to determine elemental composition (O and C ratios) and high-resolution spectra from 280 to 300 eV to analyze C. For the quantitative analysis, the spectra were baseline corrected, normalized, and curve fit using IGOR Pro 5.05 software (WaveMetrics, Inc.). The area of each peak identified by curve fitting was mathematically computed (Fabiya et al. 2009). The following data processing restrictions were made: (1) the full widths at half height (FWHM), for C1 (C–C or C–H), C2 (C–O), C3 (C=O or O–C–O), and C4 (O–C=O) peaks (285, 286.5, 288, and 289.5 eV) were kept constant (1.6 eV); (2) the fitted peaks were made using Voigt; (3) the third restriction is that a peak C0 (C=C), at 283.5 eV, was fitted when the residual of the band indicating the presence of this peak (FWHM of 1.6 eV); and (4) therefore, with these restrictions in place, a peak-fitting routine was then used to minimize and randomize the residual signal.

Results and discussion

Analysis of wetting by water performed on the modified and unmodified materials (Figs. 1, 2) clearly showed that surface wetting of the substrate had been significantly reduced. So, the initial contact angle of the butyl acrylate (BA) and butyl methacrylate (BM) modified material at 103 °C increased to above 100° while that of the controls subjected to surface heating only remained at ca. 90°. A similar effect can be observed for the series modified at 180 °C; however, the increase in

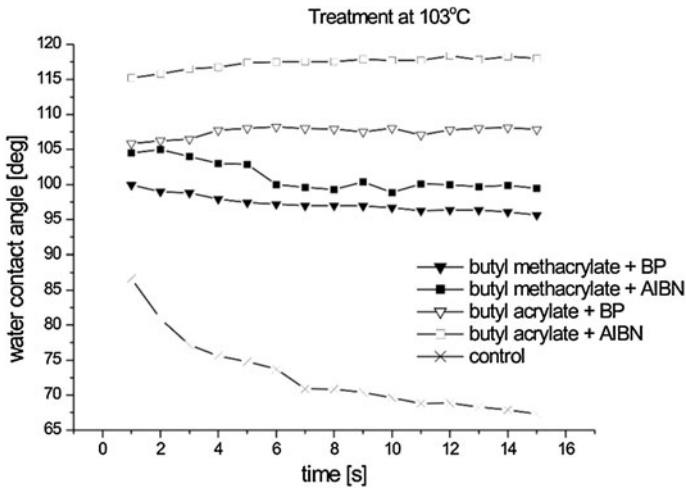


Fig. 1 Water droplet spreading over the materials modified with butyl acrylate and butyl methacrylate at 103 °C

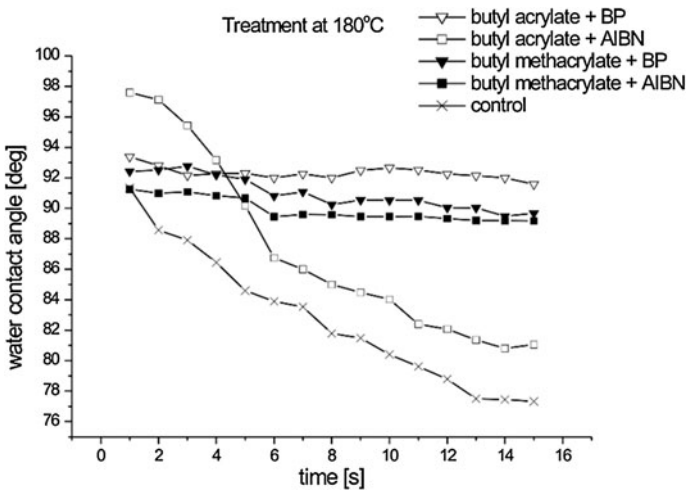


Fig. 2 Water droplet spreading over the materials modified with butyl acrylate and butyl methacrylate at 180 °C

contact angles was lower. Not only were higher contact angles observed, but also they hardly changed within 15 s of measurement (Fig. 1). Thus, it is clear that in all cases, surface wetting of the materials was altered and decreased.

FTIR spectra

From the FTIR spectra shown in Fig. 3, it is clear that polymerization reaction performed at 103 °C with AIBN as initiator was effective, since an increase in

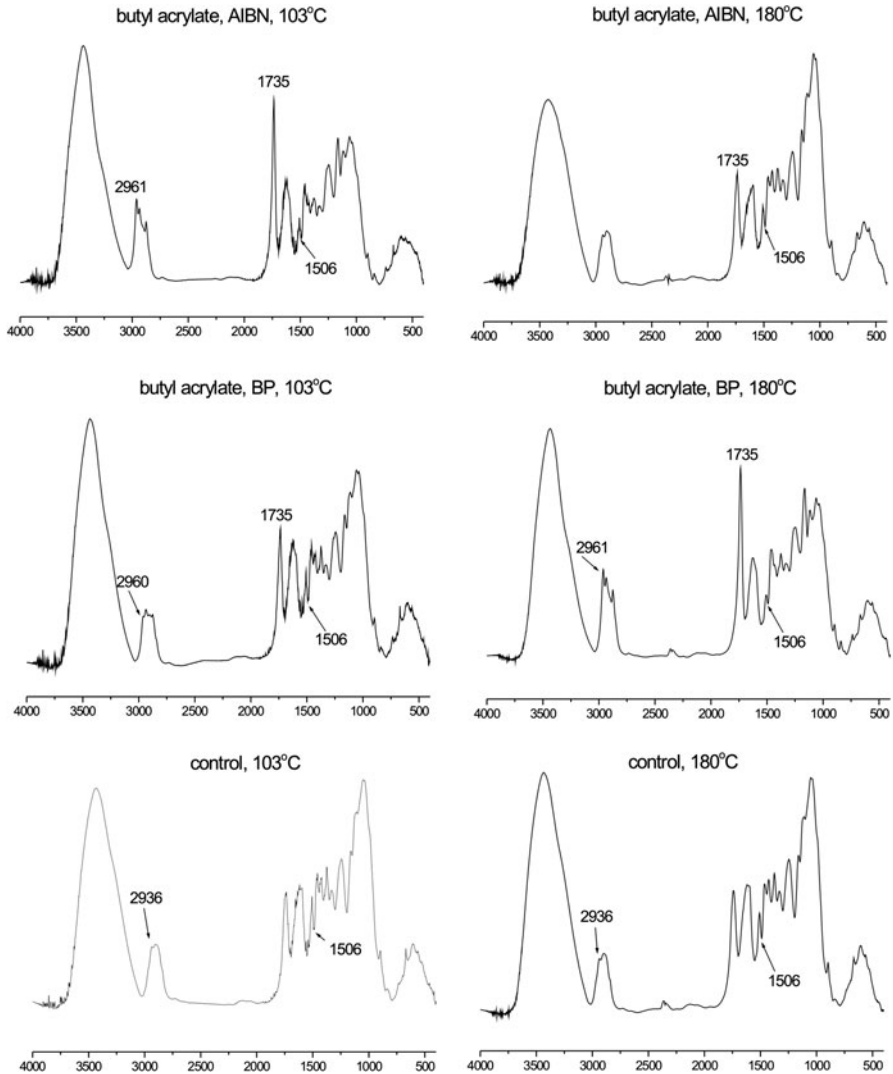


Fig. 3 FTIR spectra of the butyl acrylate (BA) modified beech wood

2,961 cm^{-1} peak intensity, which is ascribed to aliphatic chains, significant ester (1,735 cm^{-1}) band intensity increase as well as a decrease in the lignin band (1,506 cm^{-1}) proving loss in lignin content can be observed (Dodson et al. 2009). However, the changes are not so obvious for the material modified at 103 °C with benzoyl peroxide (BP) which requires higher decomposition temperatures, and thus, the observations remain coherent.

On the other hand, changes on the spectra of the material modified at 180 °C with butyl acrylate–benzoyl peroxide system (Fig. 3) suggest that benzoyl peroxide gave

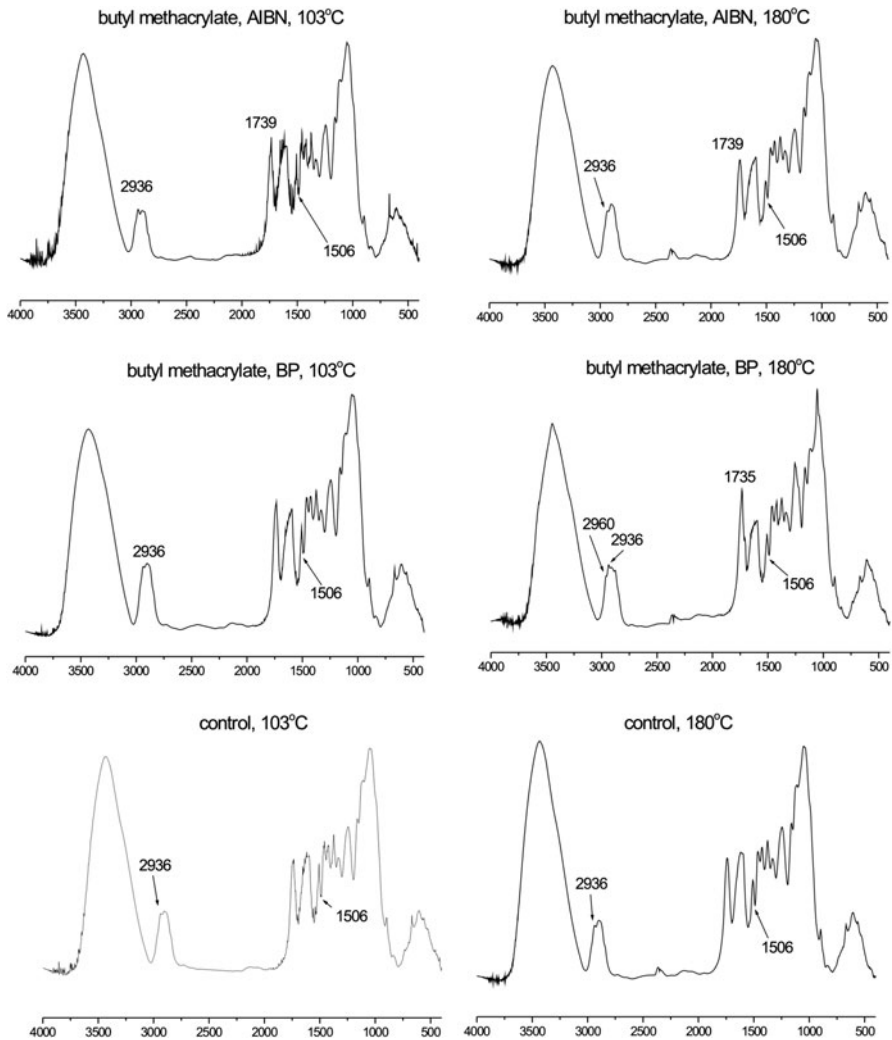


Fig. 4 FTIR spectra of the butyl methacrylate (BM) modified beech wood

higher yield of the polymerization, since higher intensity of peaks at 2,961 and 1,735 cm^{-1} as well as loss in 1,506 cm^{-1} band can be observed.

FTIR spectra of butyl methacrylate (BM) modified materials are shown in Fig. 4. As it is indicated, the intensities of the peaks at 2,936, 1,739 cm^{-1} and lignin band at 1,506 cm^{-1} were not altered as much for butyl acrylate (BA). However, the spectra suggest some yield of the reaction; especially, the band at 2,960 cm^{-1} should be noticed, since it occurred for butyl methacrylate–benzoyl peroxide system at 180 °C, as well as increased intensity of the band at 2,936 cm^{-1} . These observations show that butyl methacrylate–benzoyl peroxide system works better at higher temperatures than AIBN does. Also, a decrease in the lignin peak at

1,506 cm^{-1} noticed for both initiators at 180 °C confirms that the reaction took place and a loss in lignin content can be seen. The differences between efficiency of butyl acrylate and methacrylate can possibly be ascribed to the slight steric hindrance occurring in butyl methacrylate.

Color changes

The final color changes of the material resulted from the treatment were analyzed. The results are tabulated in Table 1. Since it is known that positive change in ΔL denotes lightening, while negative change denotes darkening, one can see that in all cases the modified material darkened—including control series subjected to surface heating only. As it is indicated, the values of ΔL for the series treated at 180 °C are higher than those for 103 °C and remain comparable even for the controls, so that the color change seems to be an effect of temperature rather than of the vinyl monomers polymerization. Total color change (ΔE) values shown in Table 1 were higher for the controls treated at 180 °C than those treated at 103 °C. Moreover, very low ΔE values were observed for the respective modified specimens. These observations show the dominant effect of the temperature which had been well documented in the literature (Ahajji et al. 2009; Esteves et al. 2008; Windeisen et al. 2007).

Hardness

The data in Table 2 indicate that polymerization of the monomers within the substrate reduced its hardness by 20 and 27 %, respectively, for butyl acrylate and butyl methacrylate initiated with benzoyl peroxide, while those monomers initiated

Table 1 Color changes of the modified materials: ΔL change in lightness, ΔE total color change

Series	ΔL		ΔE	
	103 °C	180 °C	103 °C	180 °C
Control ^a	−6.55	−21.01	8.88	21.76
BM + AIBN	−5.49	−20.73	4.48	0.47
BM + BP	−1.83	−22.14	5.90	1.50
BA + BP	−12.96	−19.85	7.34	1.87
BA + AIBN	−11.74	−26.61	5.31	5.91

^a The values are differences between the controls subjected to surface heating only and raw untreated zero references

Table 2 Brinell hardness of the modified materials

Monomer	Initiator	HB (kG mm^{-2})
Butyl acrylate	Benzoyl peroxide	49.2 ± 10.6
	AIBN	34.2 ± 1.1
Butyl methacrylate	Benzoyl peroxide	53.5 ± 9.3
	AIBN	35.5 ± 1.0
Control		66.8 ± 10.4

with AIBN decreased hardness by ca. 50 %. Significant loss in that parameter might be explained by plasticizing effect of the poly(butyl acrylate) and poly(butyl methacrylate), since measurement temperature (25 °C) was above their glass transition temperatures -49 °C and $+20$ °C, respectively.

SEM analysis

The alternation in the modified material caused by the contact heating in the presence of the monomers is shown in Fig. 5. Due to the substantial volume of the monomers applied onto the material, lumens and vessels of wood were filled and subsequent polymerization within pores occurred. Hence, it seems that exact wood grafting with vinyl monomers cannot be achieved using the proposed approach, but instead only a bulk polymerization within the wood pores occurs.

X-ray photoelectron spectroscopy

XPS results are of particular interest because it is a true surface technique; the chemical composition of only the top 1–20 nm is analyzed (McDonald et al. 1999). This allows a very thin polymer coating to be detected without interference from the bulk properties of the material. The results obtained from XPS analysis (widescans) for the control and modified beech materials showed only the presence of carbon and oxygen. The peaks for C_{1s} and O_{1s} had chemical binding energies of approximately 285–290 and 532 eV, respectively. According to Mjorberg (1981), the C/O ratio for cellulose and lignin is 1.20 and 2.77, respectively. The beech

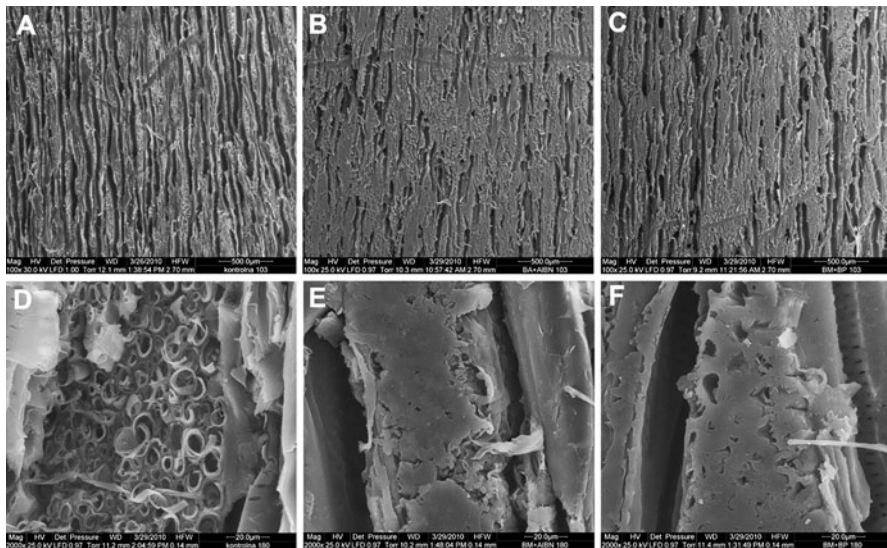


Fig. 5 SEM images of the modified wood: **a** control 103 °C, **b** butyl acrylate + AIBN at 103 °C, **c** butyl methacrylate + benzoyl peroxide at 103 °C, **d** control 180 °C, **e** butyl acrylate + AIBN at 180 °C, **f** butyl methacrylate at 180 °C

Table 3 Surface composition (%) of the modified materials determined by XPS

Treatment	C0	C1	C2	C3	C4	C/O
Control 103 °C	50.6	44.5	4.9	–	–	0.56
BA + BP 103 °C	23.3	58.6	13.2	2.6	2.2	0.53
BA + AIBN 103 °C	39.1	50.2	5.1	3.1	2.4	0.83
BM + BP 103 °C	13.3	62.9	14.2	7.2	2.3	0.59
BM + AIBN 103 °C	66.3	29.7	3.6	0.5	–	0.59
Control 180 °C	1.3	47.0	39.0	7.6	5.1	0.63
BA + BP 180 °C	38.1	54.5	2.8	4.6	–	0.53
BA + AIBN 180 °C	40.9	49.7	6.6	2.7	–	0.91
BM + BP 180 °C	27.6	52.7	15.8	3.9	–	1.0
BM + AIBN 180 °C	17.0	56.4	19.4	6.3	0.9	1.0

control and modified samples have C/O ratios (Table 3) considerably lower (0.5–1.0) than that of pure cellulose and lignin. This was unexpected, but could be explained by oxidation of the material during oven drying and hot-pressing surface treatments. The experiments at 180 °C showed a general increase in C/O ratio upon grafting, suggesting that the surface was polymer coated.

In addition to C/O ratios, the relative proportions of the XPS carbon bands C0 to C4 can also be used to determine the composition of the surface. High-resolution scans of the C_{1s} region were analyzed after peak fitting (Table 3) and the spectra shown in Fig. 6. For the 180 °C beech control sample, the XPS C spectrum showed a composition of C0 + C1 (48.3 %), C2 (39 %), and C3 + C4 (12.7 %), and this shows that the surface was lignin rich (McDonald et al. 1999). This could be a result of lignin migration since the beech was treated above the softening temperature of lignin. Upon butyl acrylate and butyl methacrylate treatment, the C0 peak intensity increased and C2 peak decreased, and this is attributable to aliphatic carbons in polymers grafted to wood.

An undoubted advantage of the described approach is its rapidity which makes the procedure less time consuming when compared to typical heat treatment. Moreover, it might possibly be suitable for rapid wood grafting with a variety of modifying agents polymerizable in free radical reactions. Thus, further research should be aimed at the alternative monomers—possibly those from renewable resources—more efficient modification conditions, initiators, and eventual photo-initiated grafting.

Conclusion

It was shown that the described procedure involving wood modification with vinyl monomers generated a material with reduced water wetting and decreased hardness, while the color of the material was not affected by polymerization itself, but resulted mainly from the surface thermal treatment. It appears that fast contact heating with hot platens—due to high heat transfer rate and high rate of radicals generated—is an

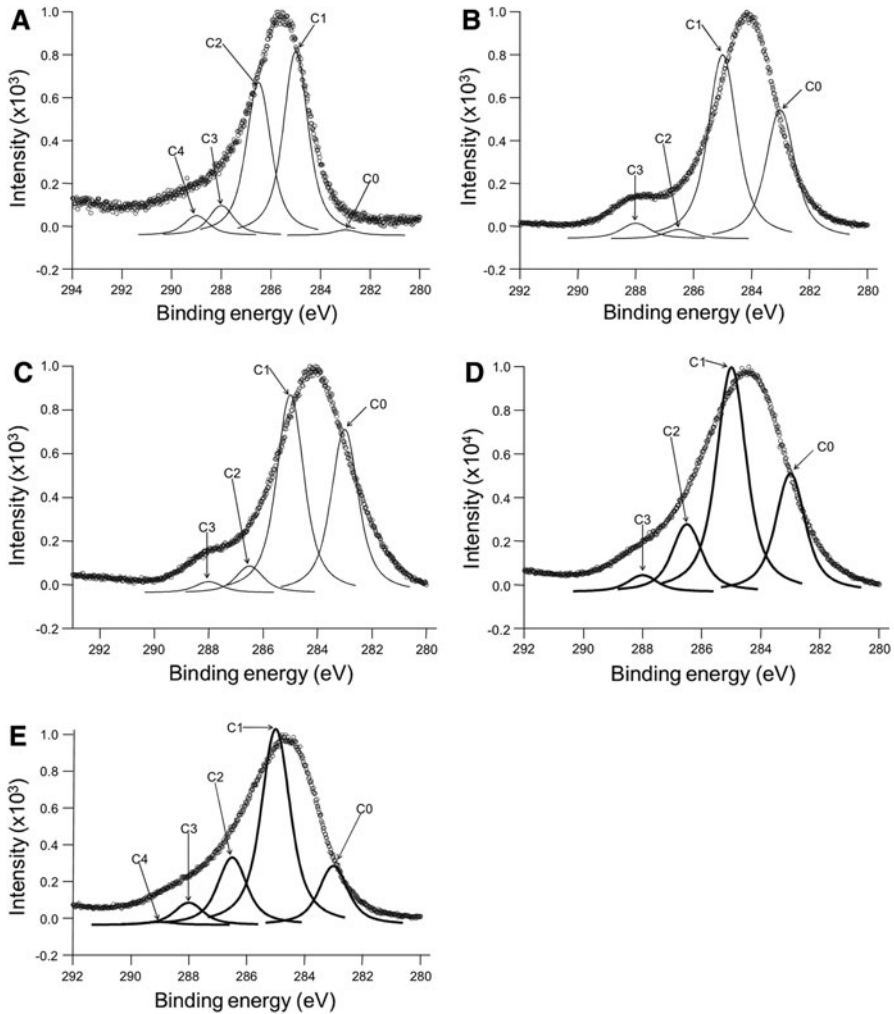


Fig. 6 High-resolution XPS spectra of **a** 180 °C control, **b** 180 °C BA-BP, **c** 180 °C BA-AIBN, **d** 180 °C BM-BP, and **e** 180 °C BM-AIBN

efficient approach for fast modification of wood. However, it must be stressed that the modifiers of high vapor pressure, for example, pinenes cannot be involved using that procedure.

Furthermore, benzoyl peroxide initiation at higher temperatures with butyl methacrylate resulted in better performing wood, while AIBN initiation worked better at lower temperatures with butyl acrylate.

It can be concluded that the proposed approach, although requiring some fine tuning (e.g., on photoinitiation or different monomers), can be potentially a procedure for rapid manufacture of modified wood.

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