Electron-Beam-Initiated Polymerization of Poly(ethylene glycol)-Based Wood Impregnants

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ABSTRACT The current study demonstrates that methacrylate and acrylate poly(ethylene glycol) (PEG) functional oligomers can be effectively impregnated into wood blocks, and cured efficiently to high conversions without catalyst by e-beam radiation, allowing for less susceptibility to leaching, and favorable properties including higher Brinell hardness values. PEG based monomers were chosen because there is a long history of this water-soluble monomer being able to penetrate the cell wall, thus bulking it and decreasing the uptake of water which further protects the wood from fungal attack. Diacrylate, dimethacrylate, and dihydroxyl functional PEG of M_w 550−575, of concentrations 0, 30, 60, and 100 wt % in water, were vacuum pressure impregnated into Scots Pine blocks of 15 × 25 × 50 mm in an effort to bulk the cell wall. The samples were then irradiated and compared with nonirradiated samples. It was shown by IR, DSC that the acrylate polymers were fully cured to much higher conversions than can be reached with conventional methods. Leaching studies indicated a much lower amount of oligomer loss from the cured vinyl functional PEG chains in comparison to hydroxyl functional PEG indicating a high degree of fastening of the polymer in the wood. The Brinell hardness indicated a significant increase in hardness to hardwood levels in the modified samples compared to the samples of hydroxyl functional PEG and uncured vinyl PEG samples, which actually became softer than the untreated Scots Pine. By monitoring the dimensions of the sample it was found by weight percent gain calculations (WPG %) that water helps to swell the wood structure and allow better access of the oligomers into the cell wall. Further, the cure shrinkage of the wood samples demonstrated infiltration of the oligomers into the cell wall as this was not observed for methyl methacrylate which is well-documented to remain in the lumen. However, dimensional stability of the vinyl polymer modified blocks when placed in water was not observed to the same extent as PEG.

KEYWORDS: electron beam • wood • polymerization • impregnation • moisture • dimensional stability

1. INTRODUCTION

Since the 1950s, electron beam radiation, involving the transfer of energy from electrons as they penetrate matter, for use in initiation of free radical polymerization has been explored enthusiastically by researchers and entrepreneurs alike (1). Although scattered studies were done before WWII, research began in earnest in the 1950s as a large amount of resources were placed into investigating the curing, cross-linking, and grafting of polymers with the use of electron beam (e-beam) technology, and hence a large amount of literature was produced in the 1960s, most notably large compilations by Charlesby and Chapiro (2−4). A large commercial source, Raychem, was established in the 1950s and full production of cable coatings and tubing was manufactured by radiation cross-linking, which is still in operation today (5). Into the 1970s and 80s, it was realized that there were difficulties in the field that caused a large degree of discouragement. This was in part due to the restrictions of only low intensities being available, leading to low penetration, and mainly positively charged α-particle-based radiation instead of the desired β-particles or electrons. These aforementioned particles have the ability to pass through thicker samples, 2.5 cm for carbon composites with an energy of 10 MeV, dependent on the density (6−8). In the past decade, however, interest has picked up because of the advantages of electron beam technology that are gaining weight in the current green technology driven environment (9−11). Further, benefits of e-beam technology include more knowledge of the processes due to computer modeling, and the development of new technology including high power industrial electron accelerators with higher output power up to 500 kWt (12). Economic factors are also driving today's research. It has been estimated by aerospace composite manufacturers that cost saving of 25−65% are possible and e-beam curing of wood adhesives are estimated to save the wood composites industry 70 PJ/year (65 trillion btu/year) (13). This cost savings is due to reduced curing times, reduced tooling costs, resin stability at room temperature because there's no need for added initiator, more formulation flexibility with multiple resins, and fibers in the same product (14).

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Currently, 1200 industrial installations provide the industries of surface coatings, tire, sterilization, wire and cable, and shrink film, however the application of this system into manufacturing lines is just beginning to be realized (10, 15).

E-beam technology is currently being used or been shown in the field of polymers to improve mechanical properties of, for example, wood polymer composites (WPC) (16), angioplasty balloons and stents (17, 18), artificial hip joints (19, 20), curing of inks and topcoats (21), polyethylene and poly(vinylchloride) heat and chemical resistance (22, 23), and chemical resistance of polyethylene gaskets and seals (24).

E-beam has also been demonstrated for use in curing conventional composites where thick samples can be cured in which much lower temperatures are reached because of room-temperature curing with the only heat generated being that of the exotherm of polymerization, making for a more controlled process and reduction of thermal degradation (25). The temperature of the exotherm can be further tuned in e-beam curing by the addition of a composite such as fibers that act as a heat sink by locally absorb in the reaction heat, and thus providing an overall lower exotherm (26). Another advantage is the high conversion found with e-beam, e.g., in studies with vinyl monomers, almost all unsaturations are reacted after cure, leading to very homogeneous and repeatable networks (27, 28), although slightly less in vinyl functional dendritic systems (29).

Further work is being investigated for wood coatings and thicker wood plastic composites (30, 31). X-rays generated by electron beam have even been used to initiate polymerization of wood impregnates to enhance properties including the durability of wood (32). Although this method has also been used in for the degradation of wood at higher doses (33), generating much heat, in another study, it was found that there was a reduction in the T_g of lignin and a change in purified celluloses thermal and moisture stability after 80 kGy e-beam exposure (34). This indicates that when using e-beam wood-modification processes, it is important to realize that both degradative and synthesis process are possible depending on the settings (33). E-beam technology is quickly being developed to aid in an increasingly environmentally friendly chemical world, with no catalyst or high-energy heat required, reducing the overall carbon footprint (35−37). This developing technology has recently been increasingly utilized by the wood modification researchers (38, 39).

Some work has been done involving the cure of acrylates and methacrylates as impregnates in wood with e-beam curing, but very little has been concluded as to whether the polymer was able to penetrate the cell wall as opposed to being present only in the lumen and if this affected the moisture sensitivity (40, 41). Further, Meyer has shown that methyl methacrylate is not able to enter the cell wall, but that poly(ethylene glycol) (PEG) readily enters the cell wall and creates dimensional stability and moisture resistance (42). This study investigates acrylate functional PEG oligomers in order to determine if penetration of the cell wall and then high conversions using e-beam can be achieved. It has not yet been explored if methacrylate and acrylate functional PEG of higher molecular weights is able to enter the cell wall and provide the characteristics that PEG alone can without leaching out because of the formation of a cross-linked network.

This study examines to which extent e-beam technology can be used to cure vinyl functional PEG oligomers in thicker wood pieces and what properties are obtained including impregnation degree, hardness, and dimensional stability of vinyl functional PEG in comparison to nonreactive PEG polymer impregnation.

2. EXPERIMENTAL SECTION

2.1. Materials. All samples were cut from the same plank of Scots Pine, *Pinus Sylvestus* sapwood with a density of 526 kg m^{-3} and a moisture content of 11%. Poly(ethylene) diacrylate (da-PEG) and poly(ethylene glycol) dimethacrylate (dm-PEG) of M_w 550−575 and poly(ethylene glycol) (PEG) of M_w 550 were purchased from Sigma Aldrich.

2.2. Impregnation Solutions. Impregnation solutions of the three oligomers, PEG, DM-PEG, and DA-PEG were prepared by mixing them with water in 0, 30, 60, and 100 wt % solutions. 0% consisted only of deionized water and 100% of only oligomer.

An example formulation of 60% DM-PEG: 180 g of DM-PEG and 120 g of deionized water.

Methods and Procedures. Figure 1 demonstrates the workflow that is further described in this section.

2.3. Vacuum Pressure Impregnation. Five replicate specimens, impregnated and then dried (NC), and five replicate specimens, impregnated, e-beam-cured, and dried (EB), were used for each of the test groups. Sets of 10 wooden blocks that had been conditioned at 65% RH at 20 °C ($w_{65\%RH}$), weighed, and dimensionally measured ($V_{65\%RH}$), were placed in 1 L autoclaves and weighed down in order to ensure homogeneous coverage of impregnation solution. It is well-known that completely dried samples of wood are very difficult to impregnate with solutions so that conditioned samples were used. The autoclaves were then placed under reduced pressure with a vacuum pump for 30 min. The impregnation solution was then added with a funnel and 10 bar of oxygen, used instead of air to reduce the risk of premature gelation. Pressure was applied for 2 h to ensure complete polymer impregnation into the blocks, observed by sawing through representative blocks. The blocks were taken out of the autoclaves and the dimension (V_1) and weight ($w_{m/p}$=WPG of monomer/polymer) calculated in which w_1 is the weight after impregnation and before drying and w_0 is the oven dry weight of the samples. This $w_{m/p}$ value is of interest because it demonstrates how much the monomer solution swells the samples (eq 1).

2.4. Moisture Content of the Unmodified Samples. Wood sample moisture content was determined according to ISO 3130. The dry 0% RH weight of the samples (a_w) was found by oven drying (48 h at 103 °C) (w_0) 5 samples from the conditioned state ($w_{65\%RH}$), gravimetri-

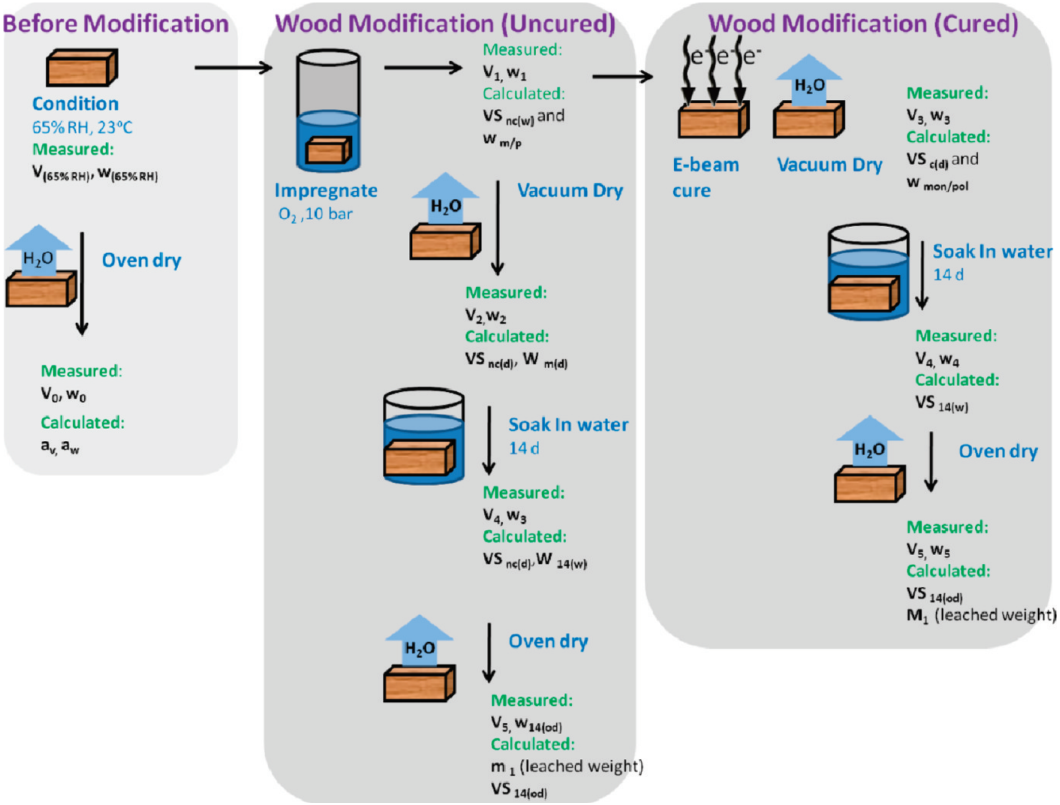

FIGURE 1. Treatment of wood blocks in impregnation, drying, and e-beam curing.

cally calculating the average moisture loss, and subtracting this % moisture from $w_{65\%\,\mathrm{RH}}$ from the rest of the samples. Moisture content was found to be 11% ± 1% (eq 1)

$$a_{\mathrm{w}} = \left(\frac{w_{65\%\,\mathrm{RH}} - w_0}{w_0}\right) \tag{1}$$

The weight increase of the samples after impregnation in comparison to the original weight, w_0, was found using eq 2, where w_1 is the weight of the samples after impregnation, but before drying

$$w_{\mathrm{m/p}} = (w_1 - a_{\mathrm{w}}/a_{\mathrm{w}})100 \tag{2}$$

The WPG after impregnation and vacuum drying ($w_{\mathrm{m(d)}}$) was found using eq 3, where w_2 is the weight after impregnation and vacuum drying the samples. The value, $w_{\mathrm{m(d)}}$, indicates how much monomer and polymer was absorbed into the wood, without the presence of the solvent

$$w_{\mathrm{m(d)}} = (w_2 - a_{\mathrm{w}}/a_{\mathrm{w}})100 \tag{3}$$

2.5. Moisture Content of the Modified Samples. The WPG after 14 days in water and corrected for polymer weight loss ($w_{14(\mathrm{w})}$) was calculated using eq 4. In eq 4, m_l is the amount of polymer that leached from the sample over 14 days, and w_3 is the weight of the wet samples after 14 days in water. The leaching over 14 days of polymer, m_l, was calculated by taking the oven-dried weight of the samples after soaking the modified samples in water for 14 d ($w_{14(\mathrm{od})}$) and subtracting this from the weight after impregnation and oven drying, but before water soaking ($w_{\mathrm{m/p}}$) (eq 5)

$$w_{14(\mathrm{w})} = ((w_3 - w_0) + w_l)/w_0)100 \tag{4}$$

$$m_l = ((\mathrm{w}_{\mathrm{m/p}} - w_{14(\mathrm{od})})/w_{\mathrm{m/p}})100 \tag{5}$$

2.6. Vacuum Oven. Half of the samples were not e-beam-cured, but directly placed in the vacuum oven for 48 h at 50 °C then weighed and the dimensions measured in order to determine the WPG of polymer and the swelling induced by the polymer. The other halves were first e-beam cured and then placed in the same vacuum oven under the same conditions for 48 h, weighed and dimensions recorded. The oligomers were not observed to volatilize under these conditions; however, the uncured samples did lose a fraction of monomer that flowed out of the wood blocks because of the reduced pressure.

2.7. Leaching Studies. Leaching studies were performed over 14 days in water according to EN 84-accelerated aging of treated wood prior to biological testing. The samples were ballasted down in water and a vacuum desiccator was used for 20 min to pull air out of the wood and allow for water penetration throughout. The water was changed a minimum of 9 times during 14 days with 5 times the amount of water to the volume of the wood sample. After 14 days, the excess water was blotted off the samples and then the samples were weighed (w_3) and the dimensions measured (V_4) in order to determine how much water was taken up dependent on treatment. The samples were then dried at 103 °C for 48 h in an oven and the weight and dimensions measured again to determine the amount of monomer leaching (m_1).

2.8. Volume Measurements. Volume was measured using pneumatic callipers, width, length, and thickness with micrometer accuracy.

The oven-dried volumes (a_v) were calculated by taking 5 samples conditioned at 65% RH ($V_{65\%\,RH}$) and placing them in the oven 103 °C for 48 h. The percent volume change was recorded and found to be around 6% (± 1%). This percentage was then subtracted from the volume of the 65% RH ($V_{(65\%)}$) samples in order to give the volume swelling coefficient $a_{v.}$

Volumetric Change. Volumetric shrinkage or swelling were found using ISO standard 4858 and 4860.

The volume swelling percent of the impregnated samples after removing from the impregnation solution and before removing the water ($VS_{nc(w)}$) was calculated in comparison to the initial oven dry sample volume (a_v) in order to determine the amount of wood swelling effect of the impregnation solutions, where V_1 is the volume of the impregnated samples before drying (eq 6)

$$(V_1-a_v/a_v)100 = VS_{nc(w)} \tag{6}$$

The volume swelling percent of the samples after impregnation and after drying ($VS_{nc(d)}$) was found using eq 7, where V_2 is the impregnated and dried sample volume. $VS_{nc(d)}$ gives an indication of how much the monomer itself swelled the wood blocks

$$(V_2 - a_v/a_v)100 = VS_{nc(d)} \tag{7}$$

The volume swelling percent of the samples after impregnation, cure, and then drying, $VS_{c(d)}$, was found using eq 8, where V_3 is the volume of the samples after impregnation, cure, and drying. This value $VS_{c(d)}$ can indicate if any bulking of the cell wall occurred or cure shrinkage occurred with cure

$$(V_3 - a_v/a_v)100 = VS_{c(d)} \tag{8}$$

The volume swelling percent of the samples after14 days in water ($VS_{14(w)}$), was calculated using eq 9, where V_4 is the volume of the wet samples after 14 days in water. This value, $VS_{14(w)}$, indicates how much dimensional stability the modified uncured and cured samples have over 14 days in water in comparison to unmodified samples

$$(V_4 - a_v/a_v)100 = VS_{14(w)} \tag{9}$$

The volume swelling % of the modified samples after soaking in water 14 days and then oven drying, ($VS_{14(od)}$) was calculated using eq 10, where V_5 is the volume of the oven-dried samples after 14 days in water. The calculation indicates the capability of the wood blocks to go back to their original modified volume

$$(V_5 - a_v/a_v)100 = VS_{14(od)} \tag{10}$$

2.9. Electron Beam (EB) Curing. EB curing was performed with a pulsed sweeping electron beam, produced by a microtron accelerator with energy of 6.5 MeV and a current of 80 mA. A total of 100 KGy dose was applied to the samples and was calibrated with a Risø calorimeter. The samples were cured in plastic bags under atmospheric conditions to prevent any evaporation.

2.10. Brinell Hardness. Brinell hardness was performed using an Alwetron TCT50 Universal Testing machine with a load cell of 5 kN with a steel ball of 10 mm and a test force of 50 kp according to standard EN-1534. Testing was done on the radial cut surface. A strain rate of 500% min^{-1}, stress rate of 250 MPa s^{-1}, and load rate of 20 N min^{-1} were used. The hardness number was calculated from the diameter of the impression left on the wood sample. The average of 10 repeat measurements was used.

2.11. FT-IR Spectroscopy. Infrared spectra in the Midregion (FI-IR) were acquired using a Perkin-Elmer FI-IR-2000 equipped with a TGS detector. Sixteen scans were averaged at 2 cm^{-1} resolution in the range of 600−4000 cm^{-1}. Samples were analyzed in duplicate using Spectrum version 3.02.01 and graphing software Origin 7.5.

2.12. DSC. The thermal properties of the samples were analyzed by differential scanning calorimeter (DSC). The experiments were performed on a Mettler Toledo DSC 820 equipped with a sample robot and a cryocooler. The DSC runs were carried out in closed sample pans sealed in air, using the following temperature program; heating from 25 to 300 °C (5 °C min^{-1}). The samples were normalized for sample weight and the exotherm in J g^{-1} was calculated by integrating the area of the exothermic peak.

2.13. Thermogravimetic Analyses (TGA). The samples were heated from 25−600 at 10 °C min^{-1} under N_2 using a Mettler Toledo thermogravimetric analysis equipped with a sample robot. The typical sample size was approximately 30 mg.

2.14. Laser Cutting Technique. The samples were ablated transverse to the fiber direction to give a cross-section using a pulsing UV (KrF) exciplex laser (Lumonix 600LX) (43) of radiation emission of 248 nm. The irradiation energy was 375 mJ, the pulse width was 20 ns, and the pulse frequency was 3 Hz.

2.15. Scanning Electron Microscope (SEM). A Hitachi tabletop microscope TM-1000 was used on low vacuum mode (LV-SEM) to image the cross-sections of the samples, and no sputtering was required.

3. RESULTS AND DISCUSSION

3.1. Determination of Polymer Conversion. To determine the efficiency of conversion of e-beam, the

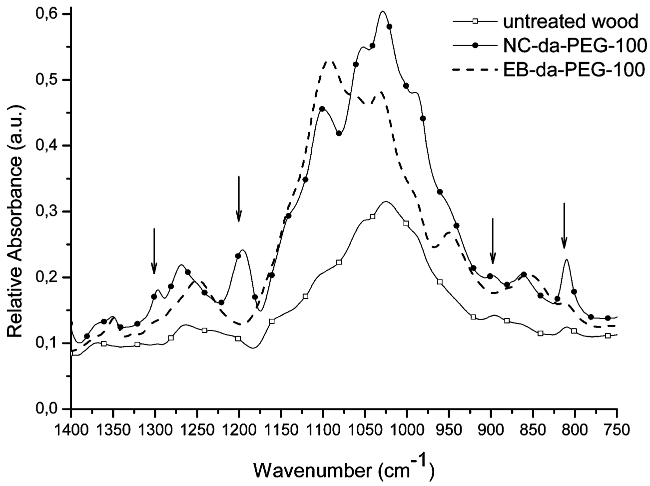

FIGURE 2. IR spectra of NC and EB-da-PEG oligomer, along with wood, NC, and EB-da-PEG samples to demonstrate chemical changes that occurred with e-beam cure, with arrows indicating vinyl reaction.

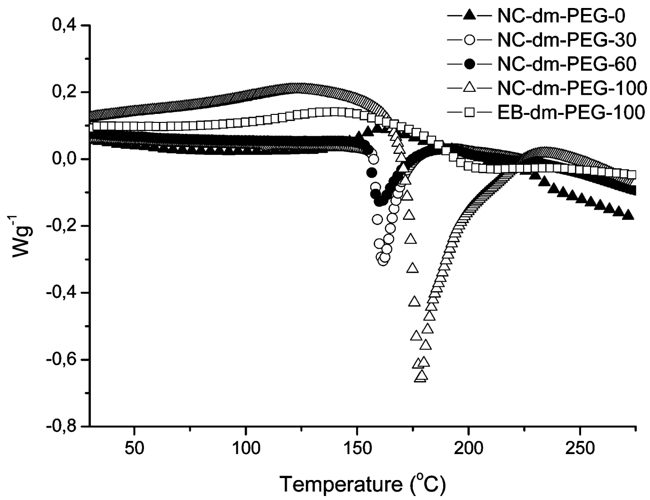

FIGURE 3. DSC spectra of NC-dm-PEG and EB-dm-PEG samples.

uncured and cured samples were measured by FT-IR to characterize the degree of acrylate unsaturation remaining. The NC-da-PEG-100 sample has bands appearing at 800, 910 1200, and 1310 cm^{-1}, because of the vinyl groups. (Figure 2.) It appears with the e-beam radiation, that the vinyl peaks completely disappear in NC-da-PEG-100 after e-beam exposure, demonstrating a high degree of cure. This high degree of cure is not common for traditional acrylate systems that typically have a characteristically low gel point. Further this demonstrates that e-beam cure is advantageous in that the material and properties will not change with time because of residual functional groups in the material.

To determine the efficiency of the e-beam cure and confirm the finding from FT-IR, the e-beam samples and uncured samples were heated by DSC in order to determine an exotherm.(Figure 3.) It was found that the impregnated samples that were uncured with dm-PEG had an exotherm proportional to the weight percent monomer where as the e-beam cured samples exhibited no exotherm. The spectrua of NC-da-PEG exhibited similar trends with similar polymerization exotherm temperatures. This demonstrates complete cure of the e-beam samples, to significantly high

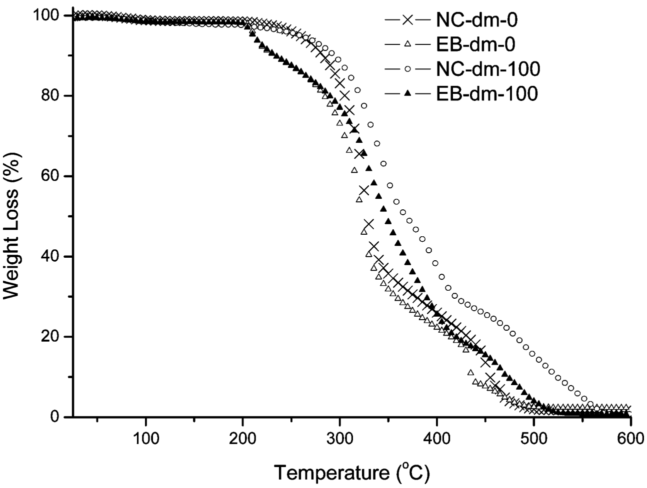

FIGURE 4. Thermal gravimetric analysis spectra of e-beam-treated and non-e-beam-treated samples.

conversion in the presence of air, without the addition of initiator. The wood itself and the PEG impregnated blocks whether e-beamed or not, showed no exotherm, confirming that the exotherm is from the polymerization of the vinyl bonds of dm and da-PEG. Further, this DSC spectrum illustrates how much energy would be needed to cure the system by thermal methods, because the vinyl oligomers do not begin to polymerize until 150 °C, as opposed to electron beam that can be performed in a matter of minutes at room temperature.

3.2. Detection of Degradation As a Result of E-Beam Energy. Both the samples containing no polymer and those containing polymer were tested by thermal gravimetric analysis to determine thermal stability changes or effects of the electron beam. (Figure 4.) It was demonstrated that both the wood sample and the impregnated wood sample that were exposed to e-beam radiation begin volatizing around 200 °C. This is around 100 °C earlier than the nonirradiated samples, providing evidence that e-beam energy has caused some degradation of the wood, creating smaller fragments and earlier volatilization. This should be investigated further in future work to ensure cure with minimal degradation of the wood. For example, this could be achieved with lower doses.

3.3. Distribution of Polymer in Modified Wood Samples. In an effort to determine the amount of polymer that has filled the lumen in ebeam modification, and determine if the cell walls have been penetrated by the oligomers, samples EB-dm, EB-da, and EB-PEG were cross-sectioned using cold laser ablation so as not to destroy the structure, and then imaged with SEM (Figure 5) The division of the cell walls can be observed in the unmodified wood sample, with the inset showing the cell structure with no lumen filled and the borders of the yearly late wood rings on the vertical sides. (Figure 5a.) This detail in the cell wall division is gone in the EB-PEG-30 sample (Figure 10b.) The gaps seen between the cell walls are evidence of rays that connect the cell walls and aid in transportation of water throughout the living tree which further illustrates the deli-

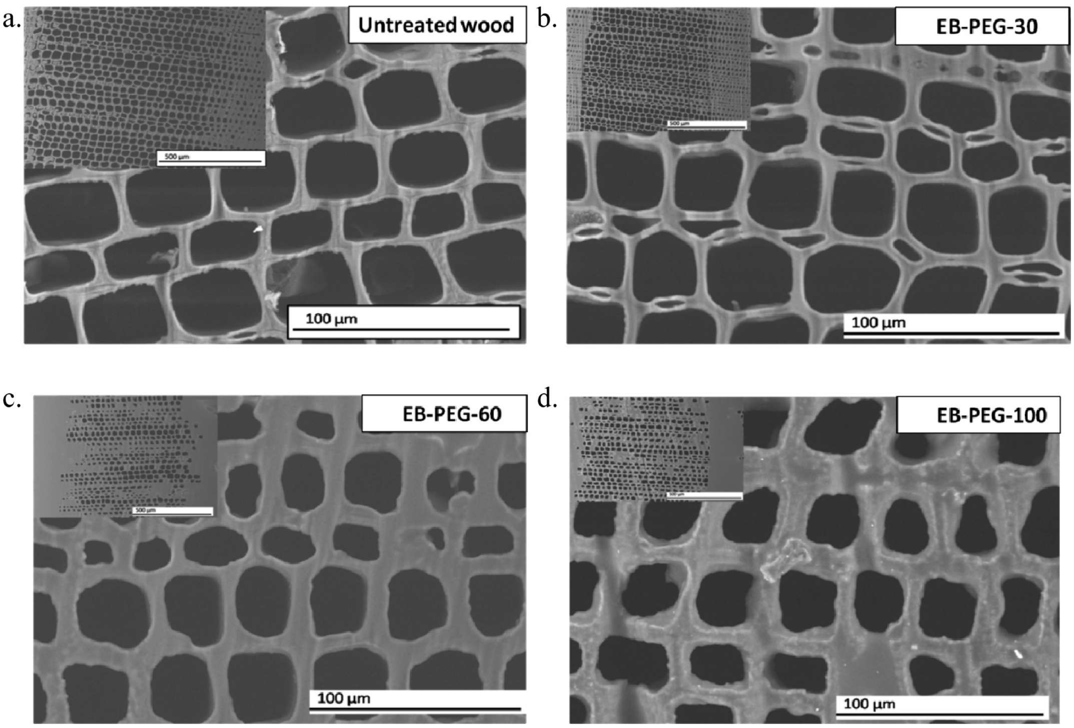

FIGURE 5. SEM images of the cross-section of (a) wood alone, (b) EB-PEG-30, (c) EB-PEG-60, and (d) EB-PEG-100 illustrating the cell wall, with the inset revealing the amount of lumen filling of the samples.

cate ability of the nondestructive method of cold-laser ablation to segment samples.

No lumen apeared to be filled by the PEG at 30 wt %. (Figure 5b.) At 60 wt % PEG impregnation, (Figure 5c.) many of the lumen begin to be filled in the latewood cells as seen in the inset on the vertical left and right. The cells begin to lose their characteristic hexagonal shape due to cell wall bulking of PEG. At 100% PEG impregnation, about the same amount of lumen filling as EB-PEG-60 and it is actually possible to see the crystallization of PEG on the wood structure, which seems not to be bound in any way and demonstrates why so much of the PEG leaches out over time. (Figure 5d.)

In vinyl oligomer-modified wood that has been e-beam-cured, EB-dm-PEG-30 shows more lumen filling that EB-PEG-30 (Figure 6a). The detail of the cell wall borders with other cells is no longer visible, indicating that there has been some penetration of the monomer into the cell walls. In EB-dm-PEG-60, there is more lumen filling observed, even more than EB-PEG-60. (Figure 6b). There is evidence of the cell walls losing their characteristic hexagonal shape, although not as extreme as observed with the nonvinyl functional PEG modification. There are also signs of polymer cure shrinkage as the lumens are filled, but the polymer has pulled away from the cell walls (Figure 6c). This cure shrinkage appears to not be as significant in the case of EB-dm-PEG-100 and this is most likely due to the e-beam curing of the samples in the wet state, leading to more moisture in the 30 and 60 wt % samples relative to 100 wt % oligomer impregnation solution and more free volume upon postcure drying.

Images of the cross-section of EB-da-PEG 30, 60, and 100 (Figure 6) appear similar to those of EB-dm-30, 60, and 100, and so images of EB-dm-30, 60, and 100 were omitted. Further, the difference in shrinkage between EB-da and EB-dm samples appears insignificant and cannot be determined from the SEM images. Although it does appear that the EB-da-PEG samples deform the shape of the cell walls a bit more, which could be the reason for increase cure shrinkage for EB-da-PEG-60 in Figure.

3.4. Effect of Impregnation and E-Beam Curing on Brinell Hardness. For an indication of the brittleness and durability, the cured samples were tested for their hardness properties and are shown in Figure 7. The uncured samples all had softer properties than the reference untreated wood and are not shown. In the case of EB-da-60, EB-dm-60 and EB-da and dm-100 have increasing hardness in comparison to the reference.

There appears to be no significant difference in the hardness after cure for the PEG modified wood blocks. These results indicate that a polymerization has occurred in the vinyl functional PEG modified samples, transforming the functional oligomers to more rigid polymeric structures. A higher hardness is normally associated with polymethacrylate in comparison to polyacrylates because of the more rigid backbone of polymethacrylate leading to a higher T_g (44).

3.5. Effect of Modification on Volume Swelling Percentage, Cure Shrinkage, Leaching, and Water Uptake. The conditioned samples were impregnated with varying monomer concentration solutions in water. After being taken out of the autoclave, the excess water was blotted off and the dimensions taken to observe the degree of swelling. (Figure 8, $VS_{nc(w)}$).

The water impregnated samples have the largest increase in volume swelling while 30 and 60 wt % show a similar

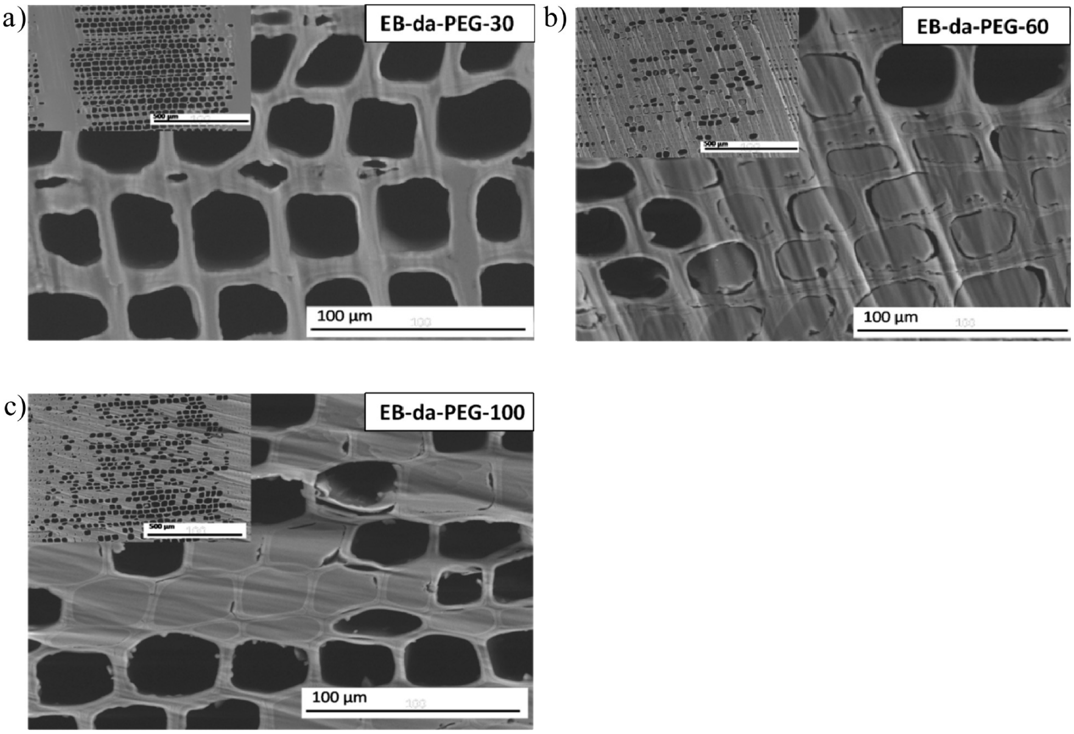

FIGURE 6. SEM images of the cross-section of: (a) EB-da-PEG-30, (b) EB-da-PEG-60, and (c) EB-da-PEG-100 illustrating the cell wall and amount of lumen fill of the samples.

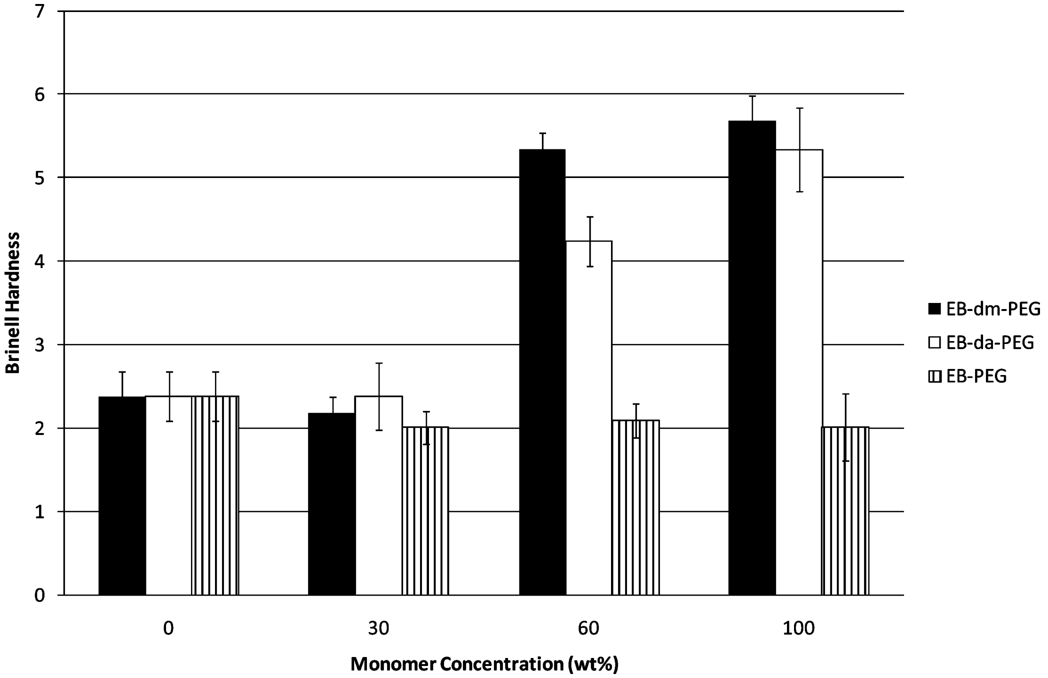

FIGURE 7. Brinell hardness of EB-cured samples, after drying in a vacuum oven for 48 h.

degree of swelling. The 100% monomer solution swells the samples the least, about 50% less than the ability of the other solutions. This is most likely due to the higher viscosity of the 100 wt % solutions in comparison to 30 and 60 wt % and due to the lack of water present to swell the wood structure. These uncured samples were then dried in a vacuum to evaporate the water in the samples and the dimensions measured again to observe how much the polymer alone swelled the samples. (Figure 8, $VS_{nc(d)}$) It was observed that in both the 60 wt % and 100 wt %, a fraction of the monomer flowed out of the samples over time because of the reduced pressure. It appears that 30 and 100 wt % polymer were comparable in their swelling while the 60 wt % was most efficient at swelling the wood samples, indicating the most efficient penetration and bulking of the cell wall. The results suggest that a significant amount of the monomers remained in the lumen in the case of higher oligomer concentrations, resulting in the observed outflow of oilgomers once the samples were placed under reduced pressure.

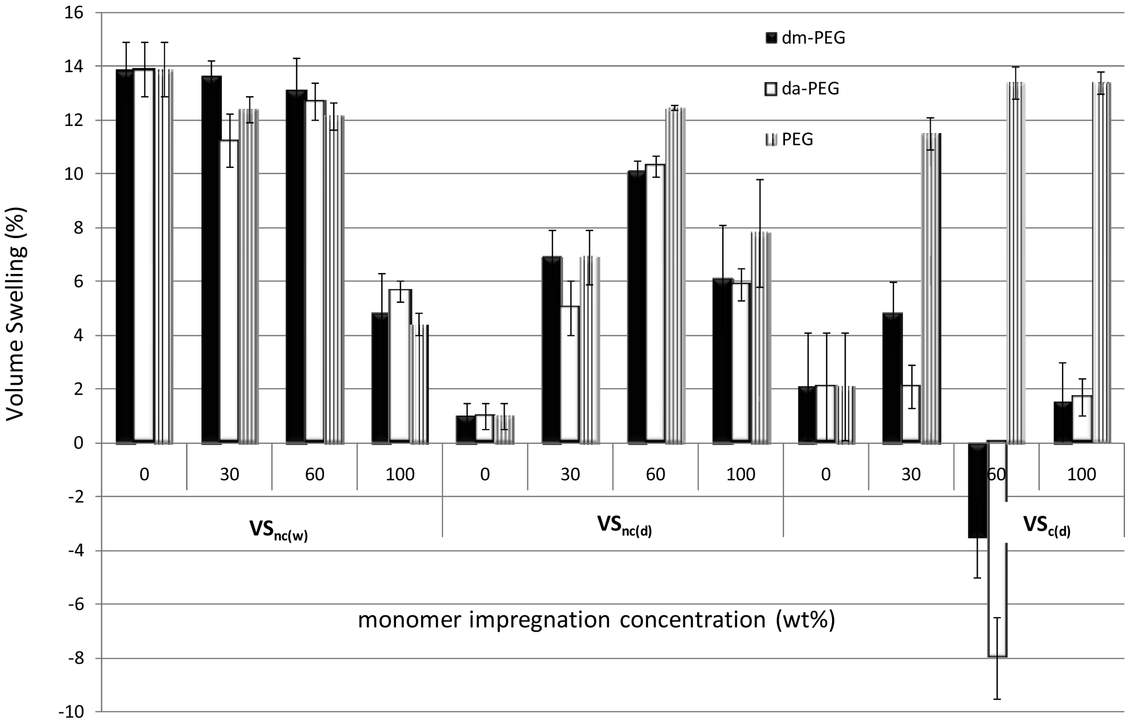

FIGURE 8. Volume swelling percentage of noncured samples taken from the impregnation solution $VS_{nc(w)}$ and volume swelling percentage after drying, $VS_{nc(d)}$, and after curing with ebeam then drying, $VS_{c(d)}$.

The samples that would eventually be e-beam-cured were also impregnated and blotted off and the dimensions measured, which gave similar results to those that were not e-beam-cured.

However, after placing the samples under e-beam energy and then drying the samples in a vacuum oven under the same conditions as the uncured samples, the dimensions were measured and showed that the polymer ability to bulk the cell wall was not observed.(Figure 2,$VS_{c(d)}$) Dimensions decreased in all samples in comparison to the uncured samples, whereas in the 60 wt % polymer, the dimensions of the samples were smaller than the unmodified blocks. This is attributed to the cure shrinkage of the polymers and implies that 60 wt % monomer is best able to penetrate the cell wall.

To determine if the shrinking effect was due to the cure shrinkage of the polymer after entering the cell wall, methyl methacrylate was impregnated into wood blocks at 100 wt % containing no water and no cure shrinkage was observed in the wood blocks. A volume swelling of 0.3% on average was observed before cure and 0.6% after cure, which is not a significant difference. This indicates that the PEG backbone in da-PEG oligomer allows the oligomer to enter the cell wall to an extent, which can not be achieved with methyl methacrylate.

The results of the volume swelling percent after impregnation but before curing or drying, reveals that the cell wall bulking efficiency depends on both the viscosity and the concentration of the impregnation solution. The cosolvent (H_2O) may also aid in the "bulking" process of swelling the cell wall, since the final content is less for 100 wt % in comparison to 60 wt % (Figure 8 $VS_{nc(d)}$). An optimum monomer impregnation concentration for the present system is most likely between 30 and 60 wt %, because 30 wt % appears to not fully bulk the samples and 60 wt % forces too much solution into the samples, because oligomer flow from the impregnated samples is observed under reduced pressure.

The result of volume swelling percent after e-beam curing reveals rather suprising results. The PEG impregnated samples exhibit similar volumes compared to the uncured samples. The dm and da samples both decreased in volume after cure where as the 60 wt % samples even exhibited a smaller volume compared to the before impregnation state. The cause of this shrinkage is proposed to be an effect of traditional cure shrinkage that occurs during most polymerization reactions. A larger shrinkage was observed for the acrylate compared to the methacrylate, which is in accordance with data on pure polymer systems where acrylates shrink more than metahcrylates (45).

Moreover, it should be noted that the e-beam-cured samples became slightly distorted when polymerized, in which the corners where pushed out as the core became narrower. This introduced an error in the volume measurments which is why these should be considered as trends rather than absolute values. It should be noted that this deformation effect caused by residual stresses that are induced upon curing could have impact on the useful service time of the wood for various applications. This is a topic for future studies.

The samples were placed in water for 14 days in order to determine the moisture content and leaching of monomer (m_1) over time. After 14 days in water, the samples were then oven-dried and weighed to determine the amount of

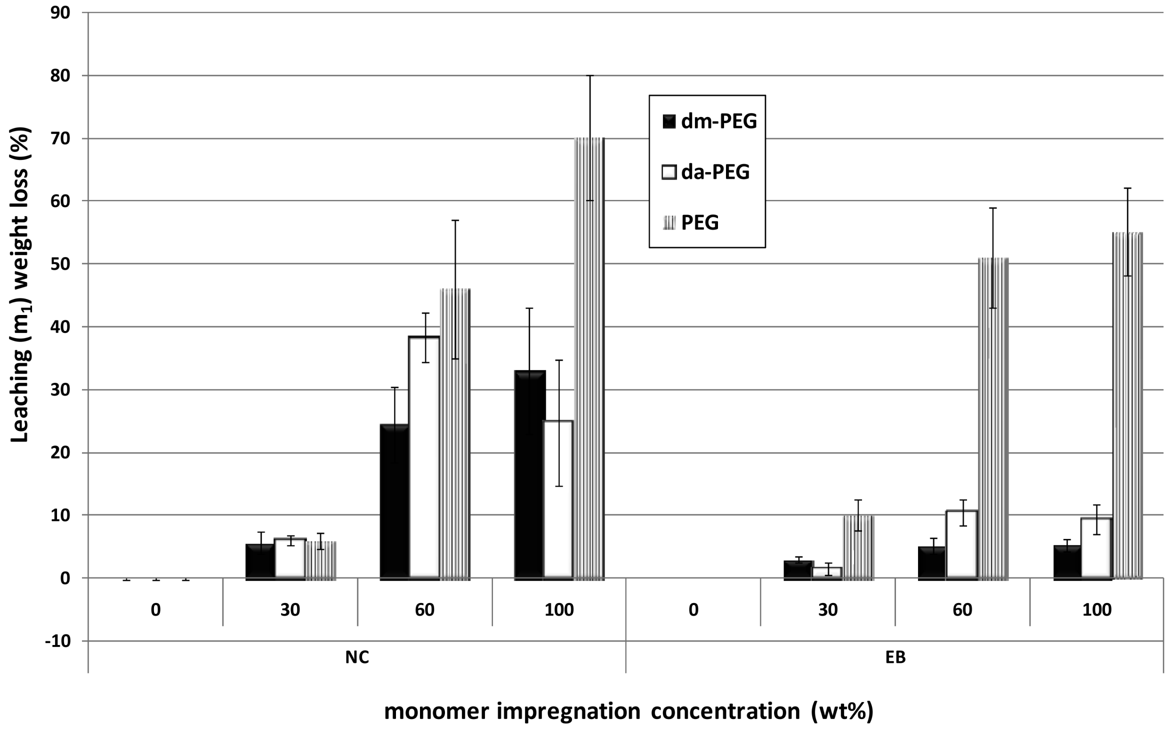

FIGURE 9. Gravimetric determination of leaching of polymer from the samples (m_1) after 14 days in water, based on polymer weight percent gain ($w_{m(d)}$).

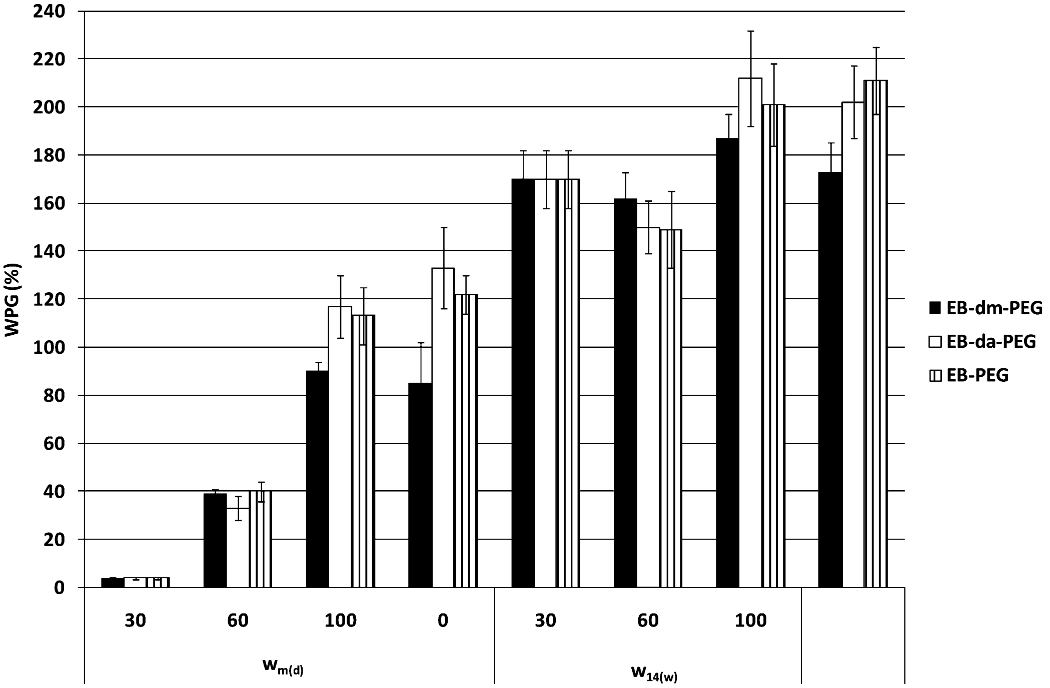

FIGURE 10. WPG of samples after impregnation and drying ($w_{m(d)}$) and after 14 days in water $w_{14(w)}$ for EB-cured samples.

polymer that had leached from the blocks. (Figure 9) The leaching of the uncured samples shows that weight loss that occurred due to monomer migration from the sample was significant and was proportional to the WPG of polymer. However, the vinyl functional samples that were e-beam-cured have very little leaching that does not significantly vary with the polymer WPG and is a bit higher than the reference wood sample. This demonstrates the ability to maintain the reacted monomers in the wood blocks by e-beam curing as opposed to the slow leaching that occurs in the case of unreacted samples.

The amount of polymer leached from the samples (Figure 9) was added to the final weight to give a true value for the weight percent gain of water ($w_{14(w)}$) (Figure 10).

The cured and uncured samples were weighed after drying in the vacuum oven to determine the amount of polymer taken up by the blocks. (Figure 10, $w_{m(d)}$) Because the uncured samples show very similar results in WPG %,

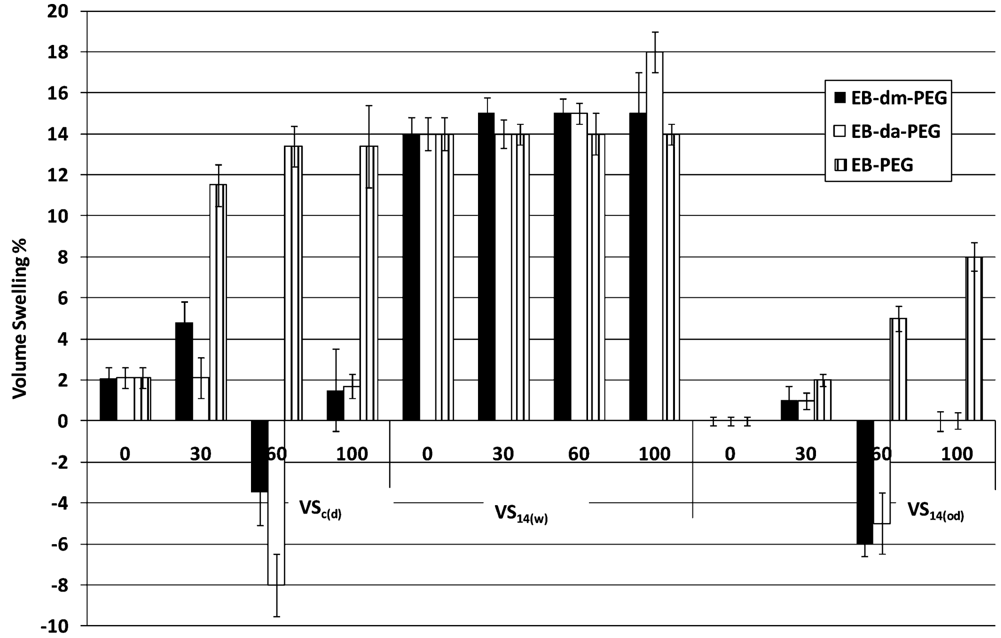

FIGURE 11. Volume swelling percentage after soaking in water for 14 days and then after oven drying, illustrating the lack of dimensional stability of EB samples.

Table 1. Naming Scheme of Samples

sample impregnated with polymer	uncured blocks	cured blocks
PEG	NC-PEG	EB-PEG
dm-PEG	NC-dm-PEG	EB-dm-PEG
da-PEG	NC-da-PEG	EB-da-PEG

these were omitted. It was found that there was a large increase in polymer uptake from 30 to 60 wt %, but from 60 to 100 wt % there was not as large a difference, which is likely due to the increased viscosity of the monomer solution at 100 wt % monomer.

The only samples shown to reduce the water uptake were the 30 wt % samples, whereas the 60 and 100 wt % samples increased in water uptake compared to the reference as a result of the affinity of PEG to bind with water by way of hydrogen bonding (46). The large degree of lumen filling of the 60 and 100 wt % samples means that the lumen chambers are filled with PEG based polymer that acts as hydrogels binding and swelling with water in the hydrated state.

To examine the degree of hysteresis and dimensional stability that occurs in dry to wet to dry dimensions of the treated samples, we determined dimensions of the wood blocks after impregnation and drying $VS_{c(d)}$, after 14 days in water $VS_{14(w)}$, and then after oven-drying $VS_{(od)}$ for uncured and cured samples (NC and EB, respectively). The uncured samples show similar behavior to the cured samples in terms of their degree of dimensional stability and therefore has been omitted for simplicity.

The volume swelling data in Figure 11 show that the PEG-impregnated samples have high dimensional stability and maintain the same volume after being in water for 14 days, whereas the vinyl oligomer-impregnated samples, whether cured or uncured, do not have dimensional stability. It can be observed that the volume swelling percent of the uncured and EB vinyl samples swells in water and then returns to the original dimensions, and decreases slightly because of small amounts of leaching, with the exception of PEG.

4. CONCLUSIONS

This study demonstrates that e-beam radiation is a viable way to cure thick wood and polymer samples (up to 2 cm). Further, the significantly high conversions of acrylates, observed by IR and DSC, is especially promising in that typical acrylate polymer conversions average around 30% and can change over time, which can greatly affect the properties and have an effect on material degradation. The amount of polymer leaching from the modified wood is also greatly reduced after e-beam curing that creates a polymer network and prevents oligomer from leaching out over time. After e-beam curing, the properties of the wood greatly improved as suggested by the large increase in Brinell hardness up to hard wood levels, which was used in this screening study as an indication of durability and toughness. It was observed by deformation of the characteristically hexagonal cell wall of Scots Pine SEM and by the cure shrinkage observed after e-beam curing that the water-soluble acrylate-functional PEG oligomers were able to enter the cell wall, but that the cure shrinkage and polymer contained in the lumen could have made the samples susceptible to a large degree of water uptake and a lack of dimensional stability in wet and dry conditions.

This research opens the door to an efficient, less expensive, and cleaner method to modify wood by e-beam radiation and to make it more durable and less sensitive to weathering. However, the modifying compounds require more investigation into the balance between water-soluble oligomers and water sensitivity of the final product.

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