Enhanced Wood Durability from Radiation-Cured Penetrants

By Anthony J. Berejka and Scott Larsen

There are more than 85 million cubic meters of treated lumber sold per year, consuming nearly 70 million kilos of wood impregnant.[1] Vacuum pressure-treated lumber has long been used to fortify wood from a variety of deleterious conditions such as fungi, wood rot, mildew and insects. Pressure-treated lumber is used for outdoor benches, planks, decking, posts and railroad ties. Pressure vessels as large as 45 meters long and greater than two meters in diameter are in use, as shown in Figure 1.

The current industry practice for preservative-treated wood consists of an impregnation cycle of (a) pulling a vacuum on the wood to de-aerate it; (b) injecting a liquid (often aqueous) wood impregnant into the vessel and applying pressure to force the impregnant into the wood; (c) pulling vacuum again to remove excess impregnant; and (d) allowing the impregnated wood to stabilize. Figure 2 illustrates a typical preservative-treated wood impregnation cycle.[2]

One of the common wood preservative treatment impregnants that had been widely used was an aqueous solution of chromium, copper and arsenic materials (CCA). These materials were shown to leach out of the wood that was adjacent to the ground causing serious toxic contamination. CCA was voluntarily removed from the market. Other aqueous materials have since been developed to replace CCA. However, the long-term durability of wood impregnated with these newer aqueous materials remains to be proven
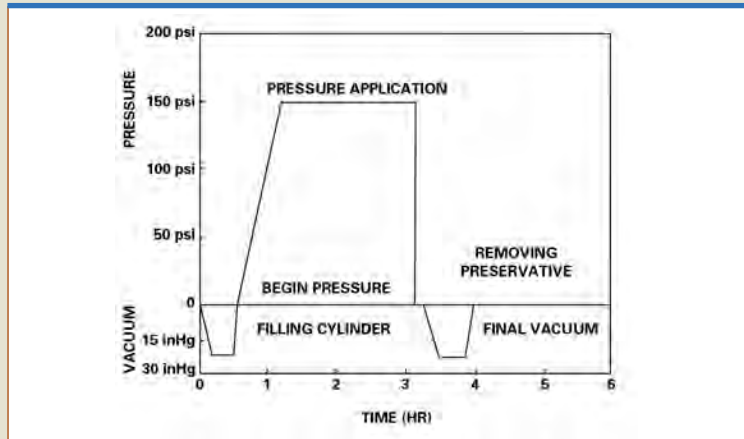
Wood treatment pressure vessels marketed by I.S.V.E. S.r.l. of Italy

FIGURE 2

Wood preservative pressure-treatment cycle

and there are other construction drawbacks. Other applications for impregnated woods for more limited markets also attained commercial use.

Radiation-Cured Acrylic Impregnants

Methyl methacrylate

During the 1960s, under the auspices of the U.S. Atomic Energy Commission, several studies were conducted using various monomers (in particular, styrene and methyl methacrylate) to impregnate different species of wood and polymerize the impregnants with radiation curing, including work done at the State University of New York, College of Environmental Science and Forestry (SUNY-ESF). Cobalt-60 was used as the radiation source for these laboratory studies.[3] This work was continued in the 1970s at SUNY-ESF and by the monomer supplier, ARCO Chemical Company (now Sartomer).[4] These studies showed that *in situ* polymerization crosslinking of monomers such as methyl methacrlyate (MMA) would fill the lumens (the tubular structures within wood used to transport nutrients

and water), but would not enter the cell walls of the cellulosic structures. Figure 3 illustrates the structure of a soft wood showing the dimensions of the lumens and cell walls.

As a result, these radiation-cured (Cobalt-60), MMA-impregnated (using a vacuum impregnation process which differs from the pressure treatment described earlier) wood products were restricted to interior uses such as long-wearing flooring, guitar necks, tool or implement handles, bows, etc. With MMA, hardness (ASTM D-785)

FIGURE 3

Structure of typical softwood

was increased, often nearly doubled depending upon the wood species and monomer loading.

Microscopic studies showed that lumen diameters for a typical softwood range from 15 to 30 nm, whereas cell wall microvoids range from 0.3 to 60 nm.[5] Given the similar electron density of wood and of the impregnating monomers, it is difficult to use transmission electron microscopy (TEM) to discern the presence of polymerized monomer within the cell wall. However, if the wood is impregnated with a silver nitrate solution, this solution can penetrate the cell walls and silver nitrate within the cell wall microvoids is clearly visible in a micrograph, as shown in Figure 4.[6] MMA, as noted, does not penetrate the cell wall and has been shown to only fill the lumens, as in Figure 5—a scanning electron micrograph (SEM).

Since wood is a hygroscopic material, it absorbs water vapor from the air and liquid water. The transmission of moisture through wood causes cell walls to swell and then contract depending upon the gain or loss of moisture. The expansion and contraction of wood places strain on the interface between wood and
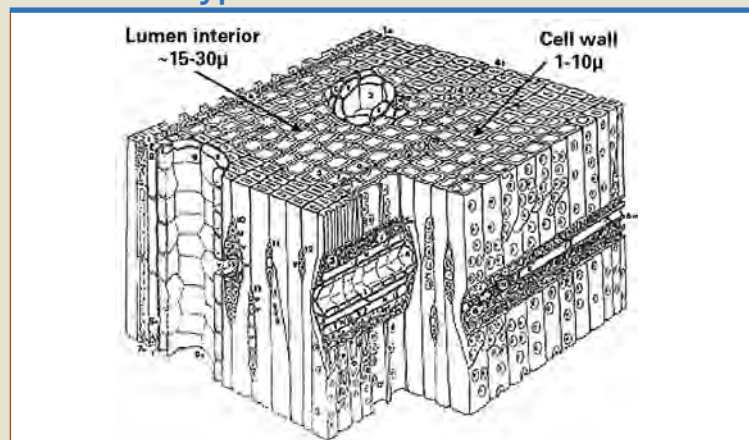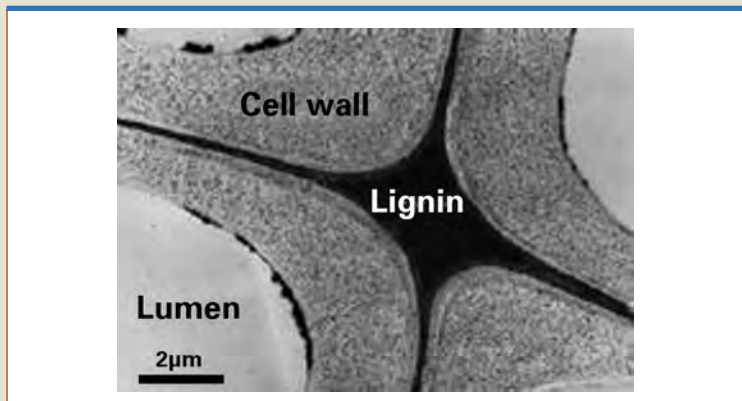
FIGURE 4

TEM of wood cross section impregnated with silver nitrate

FIGURE 5

SEM of ash impregnated with MMA at 150x

polymeric coatings, causing coatings to lift or peel.

Hydroxyethyl methacrylate
More recent investigations of radiation-curable wood impregnants conducted at SUNY-ESF showed that a hydoxy-terminated acrylate monomer, hydroxyethyl methacrylate (HEMA), would penetrate the cell walls of wood and alleviate the adverse effects of moisture exposure.[7] HEMA is slightly larger in molecular weight (Mn = 130) than MMA (Mn = 101) as illustrated in Figure 6. HEMA has a molecular

size (0.73 nm) that is small enough to permeate the 3.8 nm dimensions of the cell wall microvoids of wood.

During polymerization crosslinking, HEMA's hydroxyl group serves as a charge transfer agent. Also, HEMA can be reacted with boric acid to form a borate that exhibits enhanced biodegradation resistance. The Hansen Solubility Parameters (HSP) for HEMA are almost equal to those of water.[8,9] Figure 7 illustrates the HSP solubility domain for cellulose. The HSP for MMA, used in the early wood impregnation work, is well outside the solubility domain for cellulose.
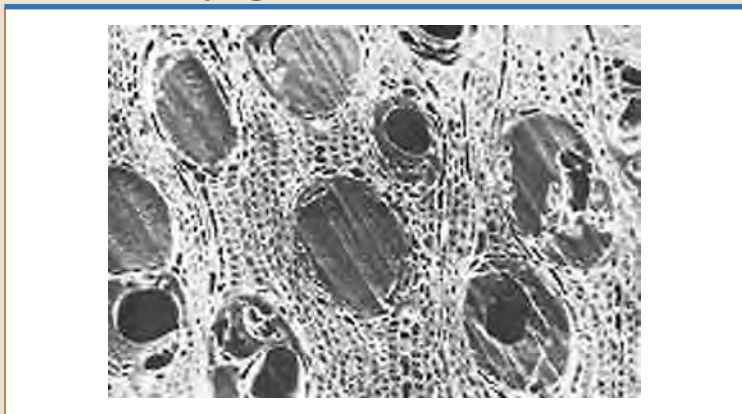
Hydroxyl groups on the surface of cellulose microfibrils and hemicellulose in the cell wall are responsible for wood's affinity for water and other polar liquids. Molecules small enough to penetrate the microvoids can enter the cell walls. However, molecular dimensions are not the only criteria. Some molecular polarity is also needed in order to penetrate the microvoids (the spaces between the microfibrils) that is to penetrate the cell walls themselves.

Radiation Sources
Instead of using radioactive Cobalt-60 as a source of ionizing radiation, electron beams and X-rays derived from electron beams were used to cure

FIGURE 6

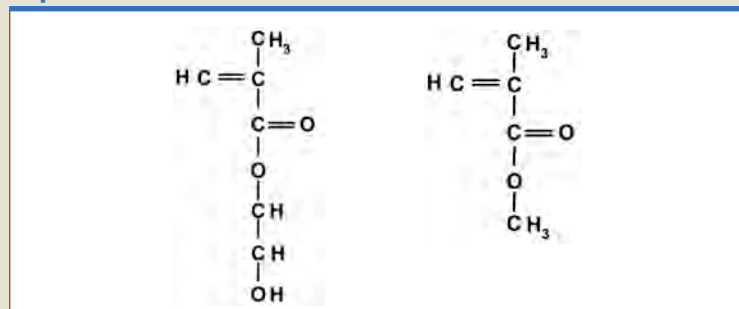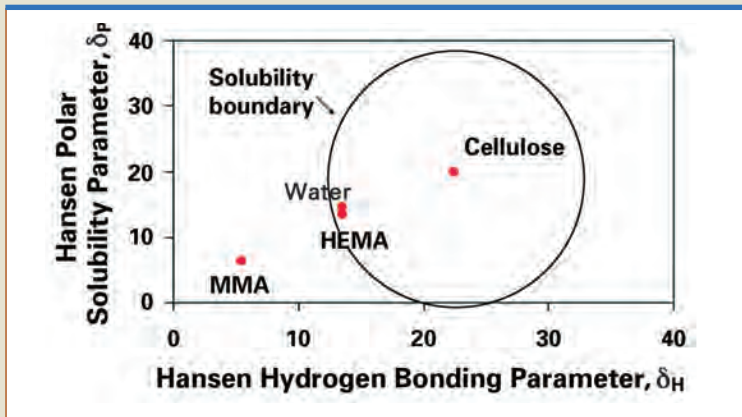### Chemical structures of HEMA and MMA monomer repeat units

FIGURE 7

Hansen solubility parameters of impregnants for cellulose

acrylate-impregnated wood. Electron beams are powered by electricity and, while they emit ionizing radiation, they do not induce radioactivity into materials at the voltages used in industry. The penetration of electron beams is proportional to the voltage of the accelerator. Industry uses accelerators ranging in energy from 80 keV (for curing of inks and coatings applied in micron thicknesses) up to 10 MeV with beam currents typically in the tens of milliamps. X-rays are generated by placing a high atomic number metal between an electron beam and a target material. Water-cooled tantalum targets have been found to be most effective. X-rays and gamma irradiation are comparable in penetration, greatly exceeding that of electron beams. Figure 8 illustrates the depth of penetration for X-rays, gamma and electron beams.[10, 11] Table I compares some basic properties of these three sources.

Radiation-Curing Studies

Initial studies involved subjecting 1 cm-thick pieces of HEMA-impregnated maple to electron beam

irradiation from a 5.0 MeV accelerator. The electron penetration at this energy is sufficient to penetrate entirely through the wood that was impregnated with the monomer. In order to avoid overheating and possible monomer volatilization, multiple passes under the beam were used. It took ~100 kGy to fully cure the impregnant. At the high dose rates of EB processing (100 kGy per second), concurrent polymerization, disproportionation and chain termination took place. Thus, a relatively high dose was required in order to fully polymerize the monomer.

Using basswood and the HEMA impregnant, 16 cm-thick blocks of wood were exposed to X-rays generated from a water-cooled tantalum target placed in front of the beam scan of a 3.0 MeV high current (30 ma) electron accelerator. Figure 9 shows the wet, impregnated blocks of wood positioned under the X-ray target.

As a result of the well-known inefficiencies of X-ray conversion (ranging from 5% to 15% output depending upon the EB voltage), this resulted in a much lower controlled dose rate of ~2 kGy/minute. The lower dose rate favored polymerization and crosslinking and minimized any concurrent disproportionation and

FIGURE 8

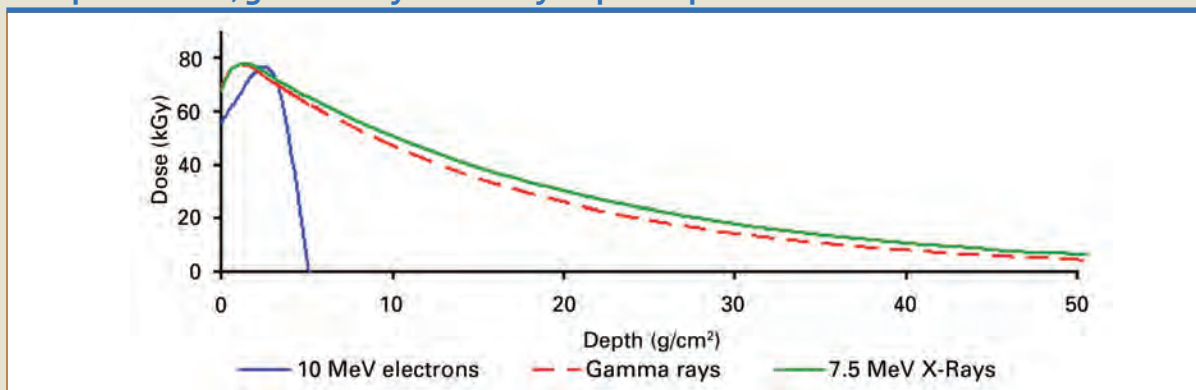### Comparative EB, gamma ray and X-ray depth of penetration

TABLE 1

Alternative sources of ionizing radiation

	Electron Beams	X-rays	Gamma Rays
Power source	Electricity	Electricity	Radioactive isotope (mainly Cobalt-60)
Power activity	Electrical on-off	Electrical on-off	5.27 year half-life
Properties	Electrons mass = 9.1×10^{-31} kg	Photons $\lambda = 3 \times 10^{-10}$ m	Photons (1.25 MeV) $\lambda = 1 \times 10^{-12}$ m
Emission	Unidirectional (can be scanned and bent by magnets)	Forward peaked	Isotropic (direction cannot be controlled)
Penetration	Finite range	Exponential attenuation	Exponential attenuation
Maximum Penetration (industrial purposes entrance = exit at unit density)	38 mm from 10 MeV	~ 400 mm	~300 mm
Dose rate	360,000 kGy/hour 100 kGy/second	960 kGy/hour 0.27 kGy/second	10 kGy/hour 2.8×10^{-3} kGy/second

chain termination. Full and thorough-cure was attained at only 25 kGy dose at the top surface. Weight loss tests showed <0.5% loss of monomer or moisture from the wood after exposure to X-rays. At this low dose, there is also minimum concern for cellulose breakdown. Lignin itself (being mostly composed of phenols) is unaffected by ionizing radiation. The X-rays penetrated the 16 cm-wood blocks,

whereas even the highest voltage industrial electron accelerators (10 MeV) would not (see Figure 8). Figure 10 shows the X-ray-cured 16 cm-thick wood block. The dark interior color indicates thorough-cure and penetration of the impregnant throughout the treated wood.

Surface temperature measurements made on the blocks while still in the beam vault were greater than

anticipated just from the X-ray energy input. Given the heat capacity of the impregnated wood, 25 kGy would impart only ~12°C rise in temperature from ambient—a surface temperature rise of more than double that was observed indicating that the controlled lower dose rate of X-rays induced an exothermic auto-catalytic polymerization of the impregnated vinyl monomer. As noted, with vinyl monomers such as small molecular-sized acrylates, the high dose rates of EB can cause competing reactions, the desired polymerization and crosslinking, and a concurrent disproportionation or scissioning of the molecule and chain termination. Lower dose rates from X-rays favored mainly the polymerization and crosslinking.[12,13]

Performance Properties

The EB-cured, 1 cm-thick wood specimens were subjected to temperature and humidity cycling along with untreated controls and controls that were not impregnated but exposed
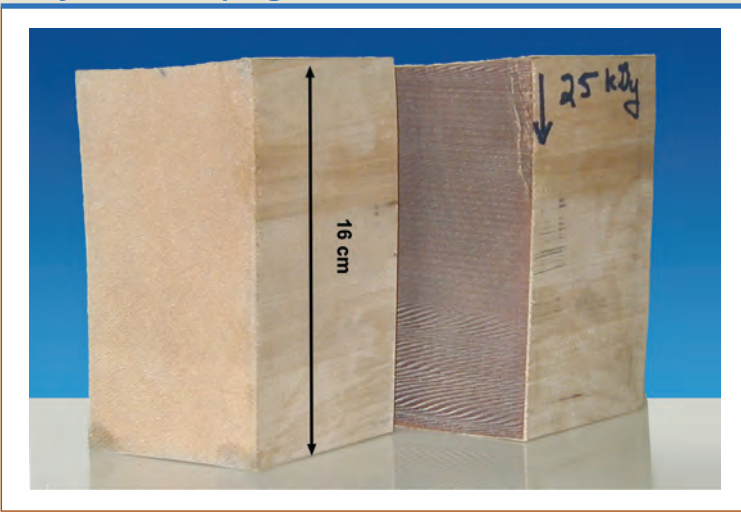
FIGURE 9

Impregnated wood under X-ray target

FIGURE 10

X-ray-cured, impregnated wood block

to the same doses. After stabilizing at an equilibrium moisture content at 9% humidity at ambient temperature, the impregnated wood samples were subjected to temperature and humidity cycling that consisted of exposing the wood to 20 days at 24°C at 78% relative humidity (RH), followed by 20 days at 21°C at 49% RH followed by 20 days at 21°C at 29% RH (60 days total). Impregnated wood cured with EB exhibited only 0.3% dimensional change in the wood or an anti-shrink efficiency (ASE) of 92.5% compared to a control of untreated wood (maple) which exhibited a 4.6% change in dimensions after temperature-humidity cycling. This indicates that the impregnating monomer had entered the cell walls and was able to stabilize the wood dimensionally from the effects of moisture vapor.

A leaching study was also conducted that consisted of immersing impregnated wood specimens in deionized water on a shaker table for eight weeks. Two sets of specimens 1 cm thick by 5 cm square were impregnated with monomer. One set was exposed to radiation and

the monomer polymerized, while the second set was not exposed to radiation and remained uncured. Only 0.03 gram of monomer was extracted from specimens exposed to radiation compared to 5.7 grams of monomer from the uncured, non-irradiated specimens.

FIGURE 11

Fungal resistance of radiation-cured wood impregnants
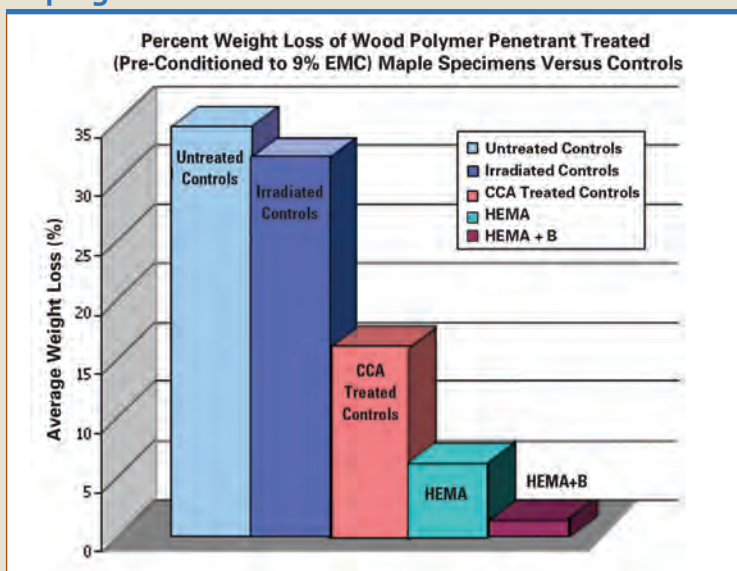

Anti-Fungal Properties

The presence of bacteria and fungi throughout the wood can cause rot when the wood moisture content is near or above fiber saturation. Many materials have been investigated to control fungal attack on wood that can lead to decay in wet wood. Toxic materials—such as the historic CCA (chromium, copper and arsenic)—have been voluntarily withdrawn by wood product manufacturers for any residential uses.

The hydroxyl functionality of HEMA was reacted with a borate salt to form a borated vinyl functional monomer. Boron, being even smaller in atomic dimensions than carbon, would not interfere with permeation into cell walls and is known for contributing to anti-fungal properties.

Controls of untreated wood, irradiated untreated wood and wood impregnated with CCA were compared to wood impregnated with HEMA and with a borated HEMA (HEMA+B). These were brought to 9% equilibrium moisture content and then exposed

to two different fungi (white rot and brown rot). The loss of weight due to fungal activity was determined. Just the HEMA itself provided a significant improvement in fungal resistance. Boration was more efficacious with one variety of fungus than another. Figure 11 illustrates the better fungal resistance of borated HEMA impregnant than just HEMA alone. Extraction tests run on the radiation-cured, HEMA-impregnated wood showed it could not be withdrawn from the wood. The borated HEMA impregnant also showed slightly better resistance to dimensional change (shrinkage 0.12%) than just HEMA alone (shrinkage 0.34%; untreated controls of the same size showed 4.59% shrinkage under the same test conditions) with an anti-shrink efficiency (ASE) of 97.3%.

Conclusion

An acrylic monomer (HEMA) has been found for impregnating wood that will enhance its dimensional stability when exposed to moisture vapor. This monomer enters the cell walls and can be further modified to enhance anti-fungal properties. When radiation-cured within the cell walls of the wood, HEMA impregnants are nonleaching and cannot be extracted.

Existing facilities can be used to impregnate the wood as well as to provide EB or X-ray curing capabilities. The complexity of the market development of this technology is being addressed. The more durable wood resulting from this treatment may minimize consumer dependence on transient materials now being used as wood coatings and surface treatments. In the long term, use of the radiation-cured wood impregnant system will prove more cost-effective. ▶

Acknowledgements

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—Anthony J. Berejka is president of Ionicorp+ in Huntington, N.Y.; Scott Larsen is a project manager with New York State Energy Research and Development Authority (NYSERDA) in Albany, N.Y.