Rapid, Low-Temperature Electron, X-ray, and Gamma Beam-Curable Resins

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- **Industry Partners:** Cytec Inc., Sartomer Company, Dow Chemical Co., Huber, and TrusJoist, a Weyerhaeuser Company.

Technology Description

- Approximately 50% of all wood used today is some type of glued-wood assembly.
- The manufacture of most glued-wood assemblies requires process heat. Process heat is required to dry the parent wood material, is used to assist in consolidation of the product (flat-pressed panel products) and is used to polymerize and cure the resin system. Drying the wood furnish materials and controlling the substrate moisture content is a major consumer of energy in the manufacturing plant.
- Thermally cured wood panels such as oriented strand board, medium density fiberboard and particleboard can be defective for lack of moisture control.

Major Wood Composite Applications

Constituent Size and Shape

- Laminated veneer lumber
- Plywood and OSB panels
- Particleboard and fiberboard
- Prefabricated wood

Limitations Remain

- Thickness is limited by heat transfer.
- Complex shapes cannot be conveniently produced.

Wood Composite Market Outlook

- **Particleboard and medium density fiberboard (MDF).** The Composite Panel Association reports more than 74 manufacturers of particleboard and MDF. US production stabilized around 1995 at about 2,000,000 m^3, but total MDF production grew 7.3% in 2003. Strong construction, remodeling, and repair markets, and residential usage are major factors. **Continued 2% growth of MDF production is expected**.
- **Structural panels - plywood and oriented strand board (OSB).** In 2003, APA-The Engineered Wood Association listed 8 US and 11 Canadian manufacturers of oriented strand board (OSB) that operated 63 North American mills. The APA also listed 34 US and 10 Canadian plywood manufacturers that operated 87 mills. **Total structural panels are expected to increase, but plywood is expected to decline**.
- **Engineered wood - glued laminated timber (glulam), laminated veneer lumber (LVL), parallel strand lumber (PSL), laminated strand lumber (LSL) and prefabricated wood I-joists (I-joist).** These products are recent innovations**.** In 2003, APA-The Engineered Wood Association listed over 50 US and Canadian manufacturers of engineered wood products that operated 90 North American mills. **This market is expected to expand rapidly.**

Energy Savings

- **Project Goal:** Development of rapid, low-temperature electron beam-curable resin systems offers **energy savings potential to the wood composites industry of 65 trillion Btu/yr at full market penetration.**
- The lower curing temperatures possible (from 450ºF to 250ºF) with beam-curing systems also offers the potential of reducing unit capital costs and double throughput.
- The minimum curing temperatures only limited by temperature needed to attain desired product density profiles. Press manufacturer believes less than 250 F required.

Other Benefits

- The lower curing temperatures possible with beam-curing systems also offers the potential of reducing unit capital costs and double throughput.
- **Lower curing temperatures will also reduce the organic volatiles temperatures thus improving the environmental aspects** of the process.
- Superior product properties can be attained. Better moisture resistance and disaster endurance.
- Much smaller press requirements needed for heat transfer.
- Extrusion techniques may allow more complex shapes to be produced.
- E-beam permits multi-material or multi-stage curing.

Projected Market

- Unit basis - 90,000 m^3/y
- First Use - 2010
- Time for 70% penetration - 20y
- 2010 market projection
  - Sheet products -   82,000,000 m^3
  - Engineered wood - 3,200,000 m^3

Energy Saving – 90,000 m^3/y Facility

Fuel Type	New Technology	Current Technology	Comments
Natural Gas (millions ft^3) Total Gas	51 135 186	96 163 259	Press 250ºF vs. 450ºF Dry Furnish to 10% higher water content
Electricity (millions kWh)	0.4		E-beam requirement
Net Savings			**Saves** 69 billion Btu/y per 90,000 m^3 or 65 trillion Btu/y at full market

Technical Barriers to Technology

- Although UV and low-energy e-beam curable resins were available for coatings, inks, and paints, no experience with high energy e-beam curable resins for wood adhesives was available. Resin chemistry, dose, rheology, and durability were unexplored for wood adhesive applications.

- Formulating the correct resin systems for even the main commodity composites, (LVL, OSB, MDF, etc), with the large number of grades and variations, and for other wood applications, including the emerging extruded or formed resin-wood composites that will likely benefit from the development of these resin systems, is almost overwhelming.

- The first commercial source built over forty years ago is still operating, so they are very reliable, and globally there are over 1200 industrial installations serving the wire and cable, shrink film, surface coating, tire, and sterilization industries. However, integration of high-energy (>1 Mev) systems into fast moving continuous production lines is only emerging. Though successful, only one prototype of a high-energy, locally-shielded continuous machine has been built.

Strategy Used to Overcome Barriers

- Based on aerospace experience to develop epoxy resins for carbon fiber composites, a large number of available chemistries were evaluated at bench scale using DMA, FTIR, boiling, etc. to classify chemical, rheological, durability, and other properties. The path to develop the develop the resins was straightforward given time and the necessary resources.

- We are producing prototypes of principal products. We are working with our industrial to evaluate best first applications. Technology viewed by industrial partners as analogous to using microwaves to preheat chips and a way to overcome current limitations.

- We are working with the IBA-RDI e-beam equipment designers and the composite machinery manufacturers that currently are supplying our industrial partners with new equipment to develop viable integration concepts.

Milestone Summary

Task Description	Planned/Actual
Survey existing wood adhesive systems	09/30/02
Evaluation of initial resin systems	12/31/02
Develop test protocol for block-tests	12/31/02
Initiate adhesion studies	03/31/03
Ethylenic and acetylinic systems	09/30/03
Downselect promising resin systems	05/01/04
Properties of glued wood assemblies	08/30/04
Evaluation of process energy balance (Go/No-Go decision)	09/30/04
Initiate testing of large sections	01/01/05
Evaluate alternative beam application methods	09/30/05
Select large-scale test sections	01/01/06
Technology transfer workshop	08/31/06
Final Report Completed (No funds carryover into FY07)	12/31/06

***Go/No-go Decisions**

The process energy evaluation was required to meet DOE criteria.

Project Objective Changes

- We have expanded the project goal to include more commercialization to the extent funding is available.
- Team is working with partners to identify a ***first application.***
- Production of commercial prototypes is ongoing.
- A technology information transfer session is planed.
- Publications and presentations are being made.
- We are coordinating interaction between e-beam designers, continuous composite-line suppliers, and continuous press designers to evaluate integration of e-beam technology into wood-composite manufacturing facilities.

E-beam Commercialization Potential

- Advantages
  - Saves energy and provides nearly instantaneous cure
  - Up to several times faster throughput possible
  - No formaldehyde and lower VOC's emissions
  - Superior durability, etc. (*e.g.* Boil test results next slide.)
  - Significant new business opportunities for **all** parties concerned. Large industrial commitment.
- Required Economic and Technical Criteria
  - Must compete in the global marketplace.
- Barriers/Facilitators to Implementation
  - Integration into large composite mills not proven.
  - Resins currently available only at medium industrial scale.
  - Intellectual property of IBA-RDI facilitates new e-beam applicator designs. (*e.g*. second slide following). IBA/RDI has offered their R&D applicator facility for on-site pressing trials as suggested by press manufacturer.

Zero Delamination of 12 Resins in 3 Cycle Boil Tests

Only 5 of 17 Resins Delaminated

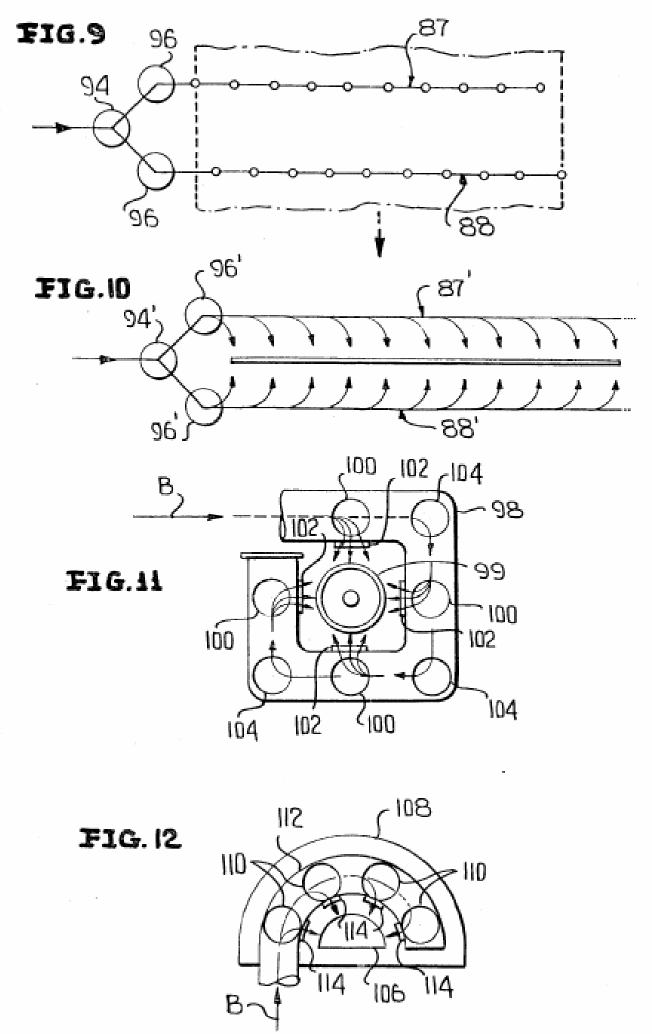
Resin	**Type**	**Cycle/Delamination, %**		
		1	**2**	**3**
R31	Aliphatic urethane acrylate	0	5	25
R33/46	Acrylate/methacrylate mixture	60	70	75
R46	Bisphenol-A dimethacrylate	30	40	75
R23	Resilient aliphatic urethane acrylate	0	75	100
R64	Diluted hard aliphatic urethane acrylate	0	15	15

Linear Beam Scanning Patent - RDI

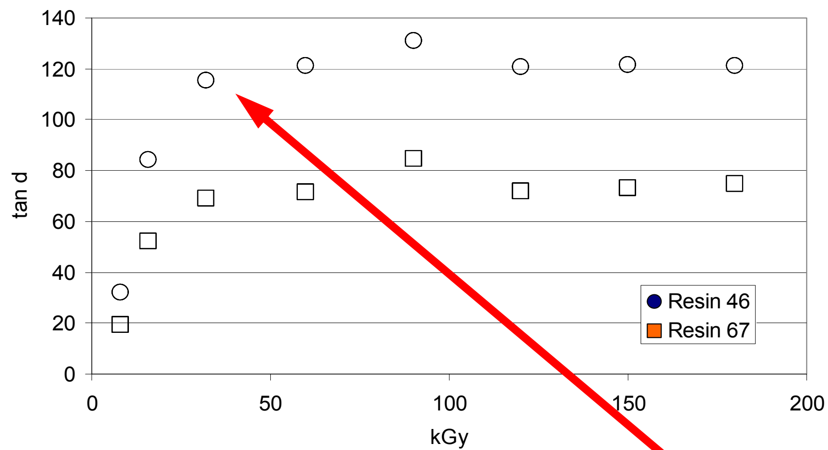
Allows virtually unlimited scan width or number of scans. No increase in height to scan long distance (>10m).

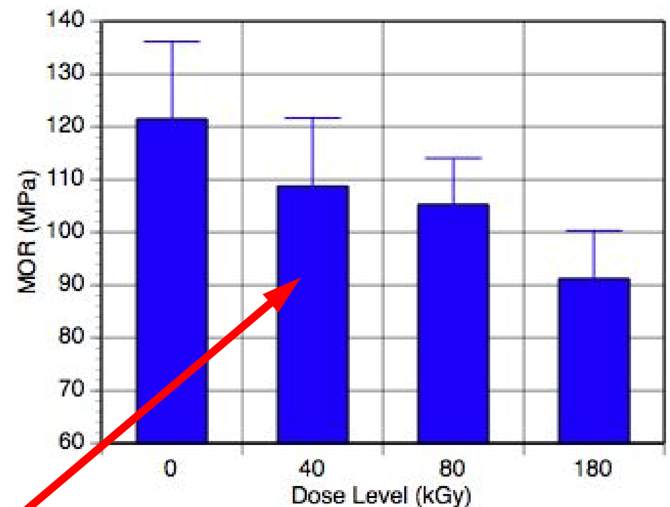
Technology now implemented.

Currently used to image entire vehicles at rest.



Optimization of Resin Cure





- Cure of resins
  - Full cure is achieved at 40kGy under ambient conditions.
  - Wood strength degradation is not significant until higher dose levels are reached.
  - Less dose will be required at wood deformation temperatures based on aerospace research.

Prototype Materials

- Prototype resins have been identified.
  - Pure resins with and without diluents and combined thermal/e-beam cure systems
  - Solid resin systems for extruded composites
- Prototype materials being developed
  - Strand and veneer composites
  - Wood-resin composites

Commercialization Plan

- The required accelerators (e-beam) are an established technology. We are working with IBA-RDI chief designers to conceptualize an integrated e-beam applicator design.
- We intend to work with our industrial partners to operate the E-beam curing system at prototype scale to:
  - Generate samples that will be used to determine the resin curing properties, product specifications and process energy requirements in a commercial setting.
  - Identify any remaining product quality, technical performance, and scale-up issues with the technology.
  - Generate process and data that will be used to perform a techno-economic assessment of the E-beam process.
  - Develop a more detailed commercialization plan for a first application.
- All of industrial partners have a a strong financial incentive to see the e-beam cured resin technology adopted across the wood industry. All of them are either the provider of the e-beam curable resins, e-beam equipment and services or a large manufacturer of wood composites. The wood manufactures would particularly benefit from the increases in productivity and lower environmental impact The commercialization of the e-beam technology would provide new markets for the resin and equipment manufacturers.

Project Partners

- Oak Ridge National Laboratory: 1) coordinates and manages reporting; 2) formulates, prepares, and synthesizes selected samples; 3) formulates resin systems and, if necessary, develops initiators; and, with other partners, 4) assesses process feasibility in terms of energy and cost.
- University of Tennessee: In conjunction with a resin chemist, 1) provides expertise and equipment for the preparation wood assemblies for resin evaluation; 2) evaluates post-cure properties, including chemistry of the glued assembly; and 3) provides facilities for resin synthesis and formulation.
- Virginia Tech: 1) provides a background in industrial processing of wood composites to assist in feasibility studies; 2) provides information on the manufacturing technologies and economics of existing wood products; 3) prepares and evaluates selected adhesive systems and wood test assemblies; 4) evaluates post-cure properties, including durability of the glued assemblies and 5) provides assistance in the selection of appropriate wood species for evaluation.
- IBA-RDI and SteriGenics International at their expense: 1) treat composite samples using e-beam systems, 2) provides consulting services on best methods for e-beam equipment design and application to industrial process lines, and 3) consults in the evaluation of resin systems.
- Other industrial partners and academic collaborators, Cytec Surface Specialties, Sartomer Company, Dow Chemical Co., Huber Engineered Woods, LLP, and TrusJoist, a Weyerhaeuser Company, provide materials, and guidance on resin selection and finished wood composite properties and requirements. M. Johnson, formerly New Business and Technical Applications Manager UCB RadcureChemicals (Now Cytec) consults on resin formulation and commercialization plans. Washington State University extruded the wood-plastic composites.

Publications

- Rials, T. G.; Dorsey, G. F.; Song, T.; and Griffith, W. L. 2003. Preliminary Investigations on the Use of Radiation-Curable Resins for Bonding Wood . Presented the National ACS Meeting, March 23, 2003, New Orleans, La.
- Rials, T. G.; Dorsey, G. F.; Song, T.; and Griffith, W. L. 2005. Radiation-curable resins for bonding wood. Presented at the 59th international Convention of the Forest Products Society, June 20-22, Quebec City, Quebec, Canada.
- Song, T. 2005. *Electron beam cured resins for wood composites*. Thesis, University of Tennessee.
- Rials, T.G., Dorsey, G. F., Song, T., Kelley, S., Moschler, W. W., and Griffith, W. L., 2005. Structure and Properties of Radiation-Curable Resins for Bonding Wood. Presented at Wood Adhesives 2005 Conference, November 2-4, 2005, San Diego, CA
- W. L. Griffith, G. F. Dorsey, D. P. Harper, W. W. Moschler, Jr., T. G. Rials Ting Song, P. M. Winistorfer, and Cheng, S., 2006. Electron-Beam Cured Resin Systems for Wood Composites, To be presented at ANTEC2006, May 6-11, 2006, Charlotte NC.
- D. P. Harper, W. L. Griffith, T. G. Rials, G. Dorsey 2006. Electron Beam Processing of Wood-Polyethylene-Acrylic Composites To be presented at the SAMPE Long Beach Symposium, May 16-20, Long Beach CA.

Summary - Significant Achievements

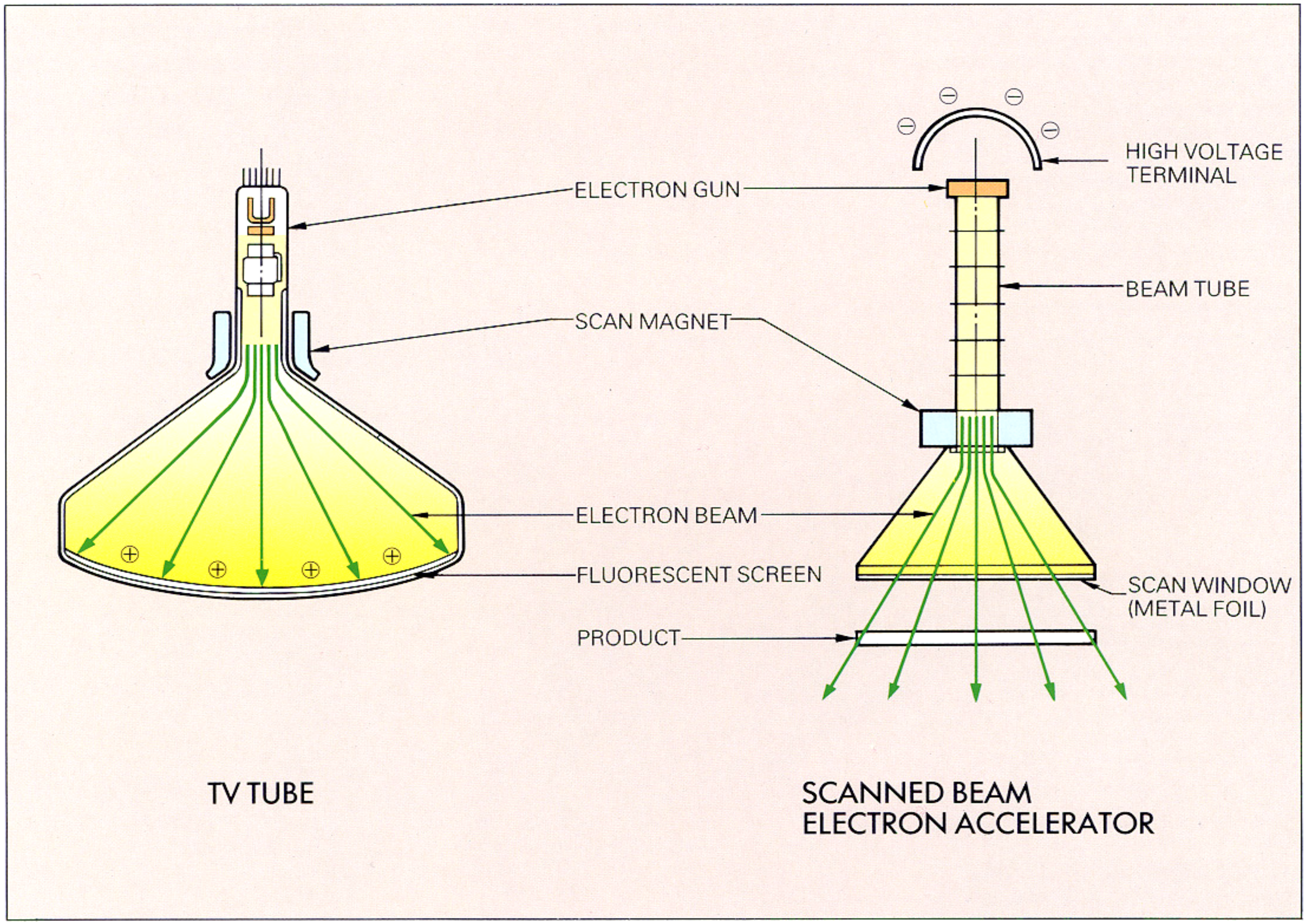
- E-beam or X-ray curable resins with strong durable bonds have been developed.
- Sheet adhesives appear feasible.
- Resins require a low cure energy.
- E-beam energy requirements much below that which degrades wood.
- Working to produce commercial prototypes.
- Working with press and e-beam designers to evaluate continuous press applicator options.

Questions?

Historical Perspective

- Softwood plywood industry established in 1905.
- Modern composite concepts developed in 1930-40's .
- Durable thermoset adhesive available in 1934 (J. Nevin).
- First OSB Plant in 1979.
- Masonite used in Hanford reactor shields in 1944.
- Aerospace e-beam epoxies developed in 1990's.
- Now >50% of wood products are glued.

E-beam Allows Precise Energy Use



E-beam Interest Derived From…

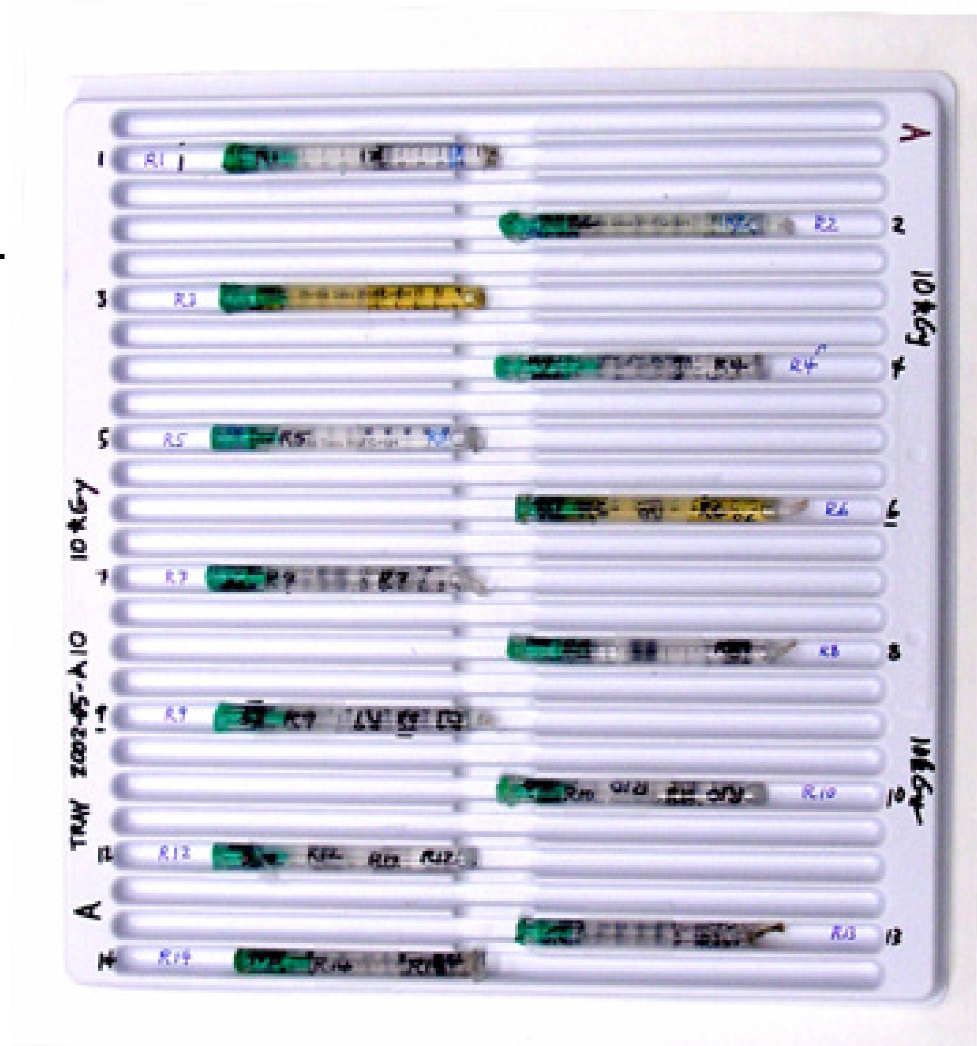
- Increased throughput (high cure rate) for both e-beam and X-ray.
- Reduced process temperature means:
  - Reduced heating time
  - Lower energy consumption and cost
  - Lower VOC emissions
  - Less product spoilage
- Improved durability of bonds
- Higher moisture content furnish allowable.
- Additional versatility for new products or optimal performance

Several Hundred Resins Evaluated

Resin Type	Functionality	Viscosity Range, mPa s	Samples
Epoxy acrylate	2	7000 to >750000	47
Modified epoxy acrylate	2, 4	26500 to >750000	13
Aliphatic urethane acrylate	2, 2.5, 3	500 to 2900000	151
Aromatic urethane acrylate	2, 2.5, 3	<5000 to 238000	17
Polyester acrylate	4, 6	630 to 48100	26
Epoxy methacrylate	2	>100000	9
Urethane methacrylate	2	1740	9
Other acrylic modifiers	1, 2, 3, 4, 5, 8	6 to >45000	189

Resin Sample Preparation

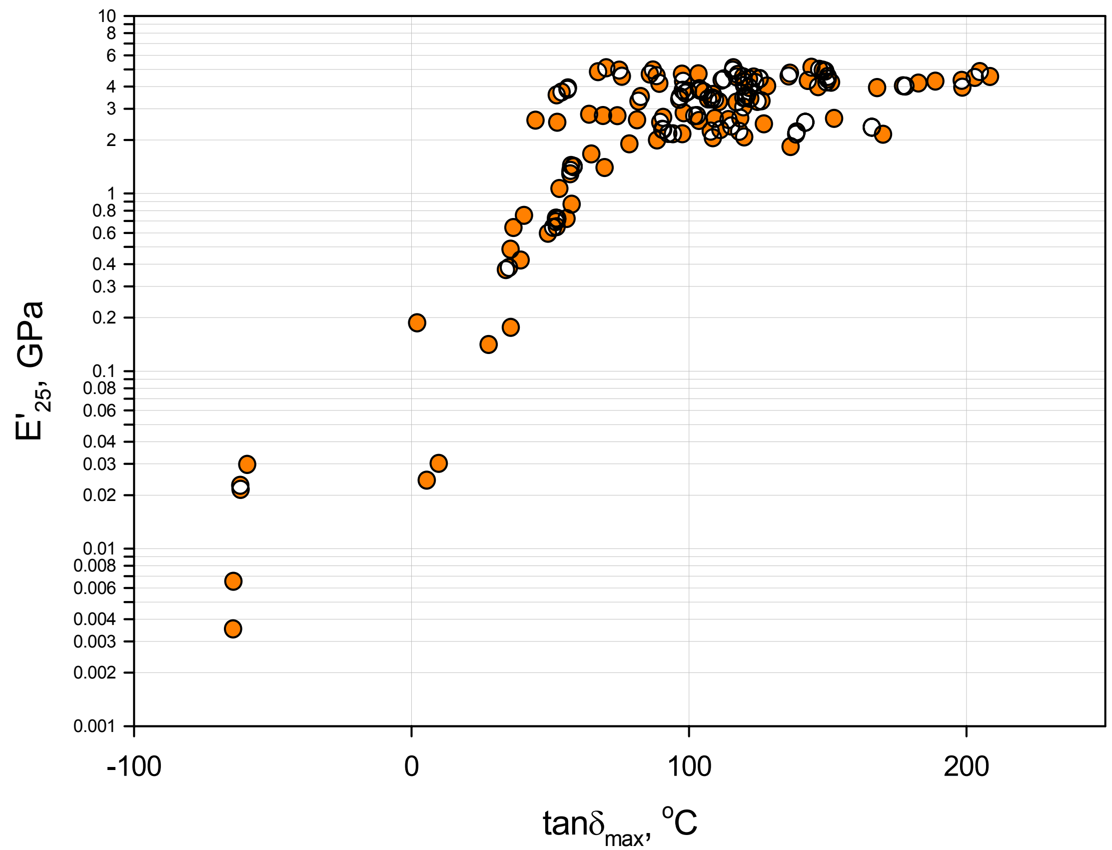
- Resin samples are prepared in 1 ml, lubricant and rubber-free syringes.
- Syringes are heat sealed and packed in covered trays.
- These samples are cured to produce uniform cylinders for materials properties analyses.



DMA Used to Measure Resin Rheology

Acrylic Property Range, DMTA

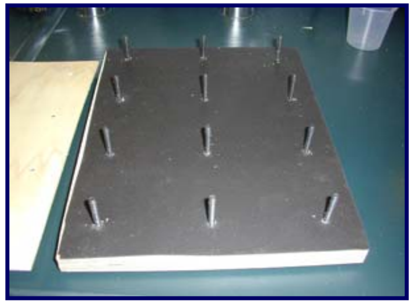
- Storage moduli ranged from 379 kPa to 6.04 GPa.
- Glass transition temperatures (T_g= peak tan δ) ranged from -64 to 208°C.
- The wide property range allows further optimization through custom blends.

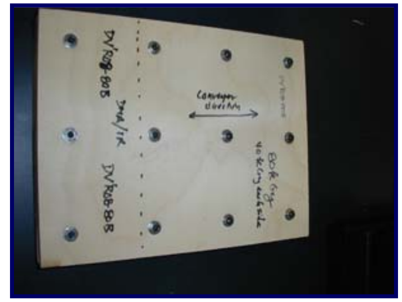


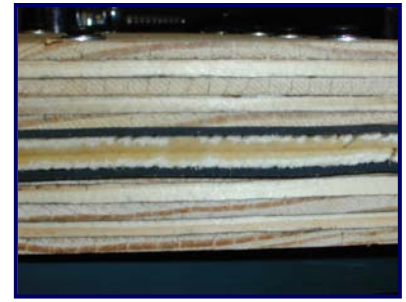
Selected Resins for Veneer Bonding Experiments

		T_g, °C		*Dynamic modulus, GPa*			
Chemical family / synonyms		**Vendor**	**Peak tan δ**	E'_{25}	E''_{25}	E'_{min}	**Tan** δ_{25}
R01	Bisphenol-A epoxy diacrylate	**67**	**128.1**	4.03	0.138	0.0893	0.0343
R07	Polyester hexaacrylate	**60**	**116.0**	5.10	0.189	0.6337	0.0370
R08	Bisphenol-A epoxy diacrylate	**91**	**143.4**	2.95	0.139	1.1379	0.0473
R09	Bisphenol-A epoxy diacrylate	**101**	**154.7**	3.88	0.161	0.2232	0.0416
R10	Bisphenol-A epoxy diacrylate	**80**	**172.7**	3.99	0.195	0.5168	0.0490
R12	Aliphatic urethane acrylate	**59**	**69.6**	1.64	0.174	0.0389	0.1066
R13	Aromatic urethane triacrylate	**82**	**122.6**	3.93	0.183	0.1359	0.0465
R14	Aliphatic urethane triacrylate	**72**	**105.3**	3.74	0.186	0.0551	0.0496
R23	Resilient aliphatic urethane acrylate		**71.0**	1.24	0.183	0.0575	0.1477
R27	Hard aliphatic urethane acrylate	**36**	**108.6**	3.61	0.182	0.0670	0.0505
R30	Hard aliphatic urethane acrylate	**90**	**155.1**	4.36	0.244	0.0924	0.0560
R31	Urethane acrylate with diluent	**87**	**203.0**	4.50	0.250	0.1985	0.0556
R36	Dipentaerythritol pentaacrylate	**90**	**25.9**	5.99	0.381	4.6547	0.0638
R40	Urethane dimethacrylate	**25**	**136.4**	4.75	0.206	0.1244	0.0433
R46	Ethoxylated(4)bisphenol-A dimethacrylate	**108**	**126.1**	3.32	0.124	0.1090	0.0374
R49	Aromatic acid methacrylate half ester		**120.9**	3.55	0.177	0.0384	0.0498
R64	Urethane acrylate blend		**177.0**	4.22	0.234	1.1168	0.0554

Almost All Formulations Showed 0% Delamination After Three Complete Boil-dry Delamination Cycles



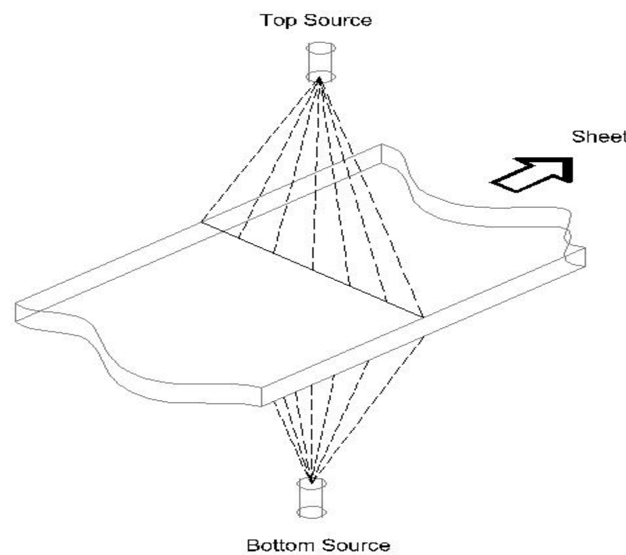




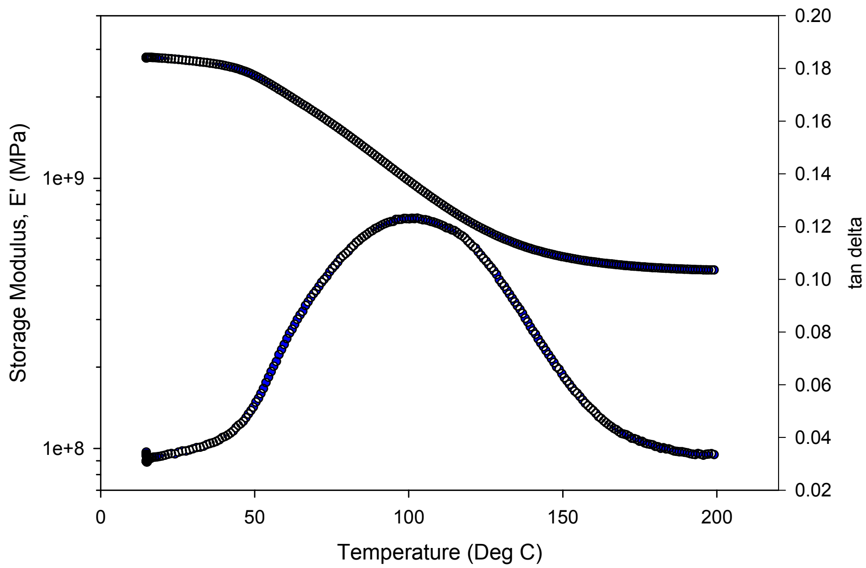
Composites were exposed to electron-beams applied to both sides of the lay-ups.

Standard test methods for shear strength and **delamination** were applied.

Selected samples were also analyzed using dynamic mechanical thermal analysis.

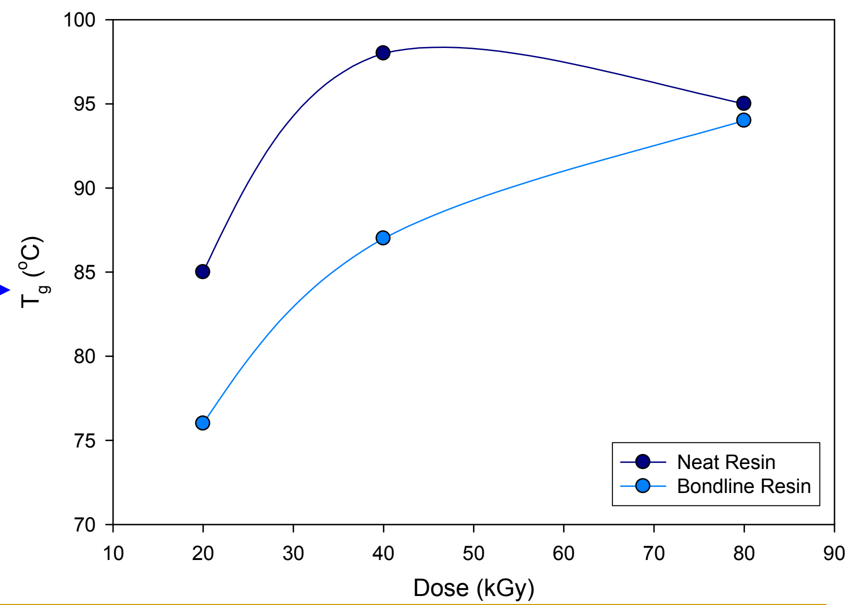


DMA of Wood Composites …



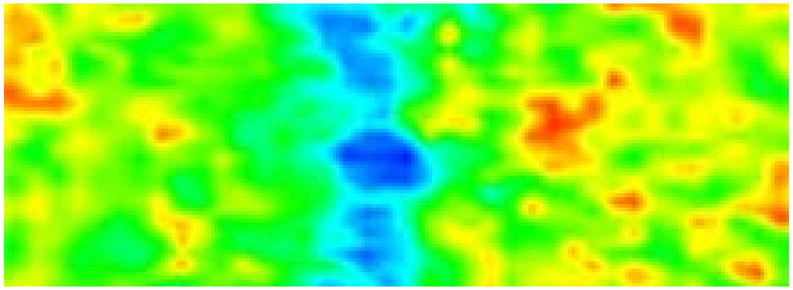
Dynamic mechanical analysis of laminate composite shows a very broad glass transition – ca. 120 C.

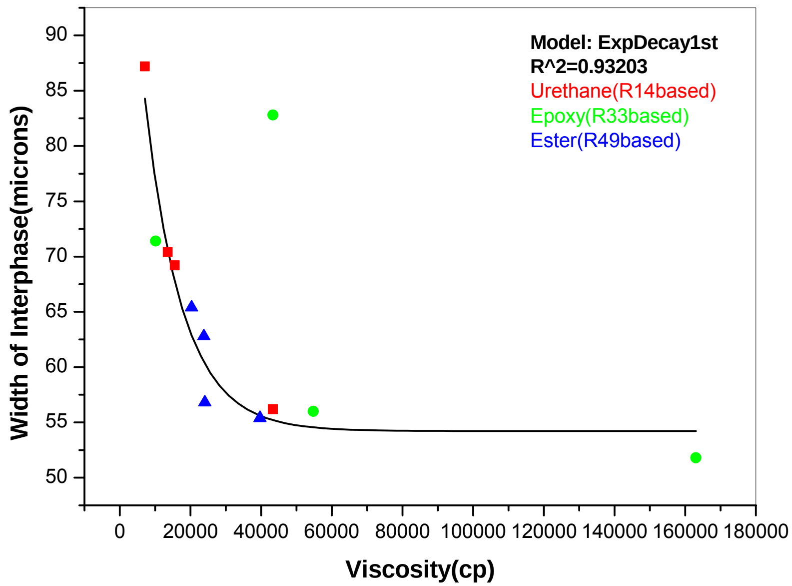
Experiments suggest some retardation of cure on the bondline, but it can be overcome through formulation.



Methods To Engineer Interphase Characteristics Have Been Identified…

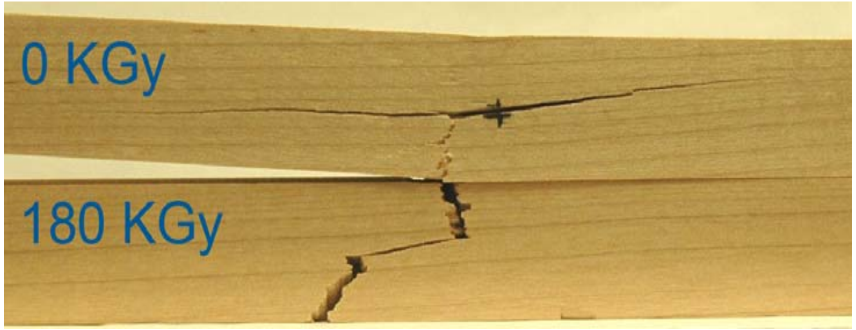
- Resin penetration impacts performance
  - Starved glue-line
  - Resin bleed out
- Penetration defined by FTIR imaging
- Convenient control afforded by designing resin viscosity

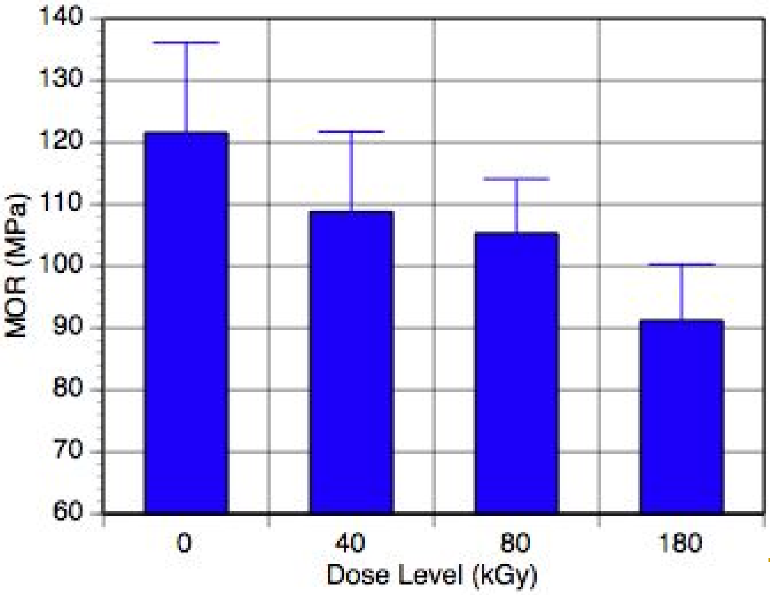




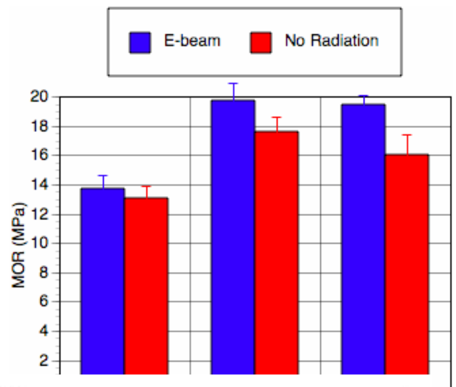
E-beam Impact on Wood

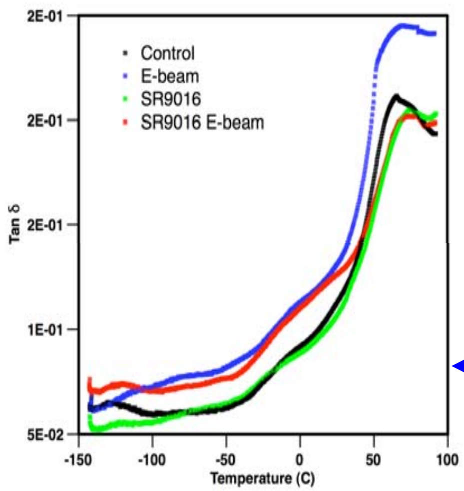
- E-beam radiation
  - No impact on stiffness
  - Brash failures at high doses
  - No significant effect on strength until dose exceeds 80kGy which is well above expected dose requirements.





Superior Wood-Plastic Composites using E-beam Resins





- Wood and polyethylene are incompatible
  - Need lubricants for processing
  - Highly filled with wood flour (60%)
- Radiation cured additives
  - Increases lubrication
  - Increases stiffness
  - Increases strength upon cure
- Improved toughness
  - Large problem in highly filled polymers
  - Increases composite durability

Moisture Absorptions of Wood-Plastic Composites

- Additive addition
  - Improves moisture performance
  - No significant difference among additives
- E-beam treatment
  - Improves moisture performance without additives
  - No significant effect between additives and e-beamed sample without additives