Chapter 24
Cellulose Graft Copolymers for Potential Adhesive Applications
Bonding of Plastics to Wood

Ramani Narayan and Christopher J. Biermann
Laboratory of Renewable Resources Engineering
Purdue University
West Lafayette, IN 47907

Michael O. Hunt and David P. Horn
Department of Forest and Natural Resources
Purdue University
West Lafayette, IN 47907

Bonding of hydrophobic plastic materials to wood to create new wood-plastic (polystyrene) materials with improved mechanical and physical properties that incorporate the desirable features of each constituent is difficult to achieve. This is due to poor interfacial adhesion between the wood and polystyrene components because of their inherent incompatibility. New, well-defined, tailored cellulose-polystyrene graft copolymers have recently been prepared using anionic polymerization techniques. Preliminary bonding studies showed that these graft copolymers can function effectively as compatibilizers or interfacial agents to bond hydrophobic plastic (polystyrene) material to wood, evolving into a new class of composites.

The concept of combining two or more unique polymers to prepare new material systems with the desirable features of their constituents is widely practiced in the polymer industry (1-5). The primary issue confronting the design of such polymer systems involves guaranteeing good stress transfer between all components of the multicomponent system. This is the only way to ensure that the components' individual physical properties are efficiently utilized to produce mixtures with the desired performance characteristics.

Obtaining good stress transfer is possible in systems where the mixture forms a miscible amorphous phase (where interphase stress transfer is not an issue);
however, obtaining a miscible phase of two chemically incompatible components is difficult to achieve. Preparing new materials by mixing two incompatible polymers results in products with reduced physical properties (6-9). Strength and toughness values are minimal and are lower for the mixture than for any of the pure components (10). This condition is due to poor interfacial adhesion between the individual components because of the inherent incompatibility.

One potential solution to this incompatibility problem that is currently practiced in the polymer industry uses block or graft polymers of the form A-B as compatibilizers or interfacial agents to improve adhesion between immiscible A-rich and B-rich phases. The physical affinity of the A portion of the graft polymer for the A phase and the B portion for the B phase serves to locate the graft polymer at the interface and physically connect the two phases through covalent bonds to the graft polymer backbone. The net result of this improved adhesion is a finer dispersion of the minor component that provides significant improvements in the mechanical properties of elongation and tensile strength (11-15).

This chapter reports successful initial efforts to bond wood in the presence of hydrophobic plastic material [polystyrene (PS)] using well-defined and tailored cellulose-polystyrene graft polymers as compatibilizers or interfacial agents. The synthesis of these tailored cellulose graft polymers is also presented.

As previously stated, the major problem confronting the development of new composite systems from wood and plastic polymers is the inherent incompatibility of the components: hydrophobic polystyrene and the polar wood-adhesive matrix. In order to create new materials with improved mechanical and physical properties, it is imperative to employ an interfacial agent like well-defined cellulose-polystyrene graft polymers. The cellulose backbone of the graft polymer is available for bonding to the wood with existing commercial resins, while the heat employed to cure the resin causes the polystyrene side chains to melt and flow into the polystyrene component of the mixture. Upon cooling, the polystyrene solidifies, creating a strong bond between the incompatible wood and polystyrene components, which are joined via the direct polystyrene to cellulose linkage within the graft polymer (Figure 1).

It may also be possible to eventually extend this bonding concept to the preparation of flakeboards and other wood-base composite materials. If plastics like polystyrene are incorporated into the composite matrix, and successful bonding between the wood and plastic is developed through the graft polymers, the three-dimensional network of plastic material throughout the composite matrix may lead to enhanced physical and mechanical properties as well as improvements in dimensional stability (Figure 2).
Figure 1. Exploded view of the use of graft polymers (GP) to compatibilize the linking of wood (W) and polystyrene (PS) materials.

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Figure 2. Continuous three-dimensional network of plastic (polystyrene) linked to wood via a cellulose-polystyrene graft copolymer. Reprinted with permission from ref. 27. Copyright 1988 Humana Press.
Experimental Methodology

Preparation of Cellulose-Polystyrene Graft Copolymers. The polystyryl mono- and di-carbanions were prepared in THF at \(-78 \, ^\circ\text{C}\) by using \(n\)-butyl lithium and sodium naphthalene as the initiators, respectively. The carbanions were reacted with dry carbon dioxide. The products were precipitated in methanol, filtered, washed with water and methanol, and dried. Size exclusion chromatography (SEC) established that the molecular weight of the polystyryl monocarboxylate was 6,200 and that of the polystyryl di-carboxylate 10,200. The mono- and di-carboxylates were reacted with mesylated cellulose acetate in dimethylformamide at 75 \(^\circ\text{C}\) for 20 h to give the cellulose-polystyrene graft copolymer (GP 1) and crosslinked cellulose-polystyrene graft copolymer (GP 2), respectively.

Bonding Studies. Test specimens were constructed of two plies of 1/8” thick yellow poplar veneer. They were conditioned in an Aminco conditioning chamber at 46 \(^\circ\text{C}\) and 12% relative humidity, which resulted in wood specimens with an average moisture content of 2.7%. All plies used in this experiment were conditioned in the chamber for at least 14 days prior to sample fabrication. Cascophen-16 (Borden Chemical, Inc.) was selected as the commercial oriented strand board adhesive to be used in the study. The resin was poured directly into a commercial paint spray gun and applied to the 1/8” wood plies using a homemade system developed by the authors. The system consisted of a small motorized cart capable of holding a cartridge of wood plies as they passed through the resin stream emitted by the stationary spray gun. The amount of resin delivered to each ply was controlled by regulating the air pressure of the spray gun and the speed of the motorized cart. Test specimens (composed of two plies) with 0.18 g resin evenly distributed across 4 sq. inches of glueline were prepared with the system. Polystyrene, graft copolymer, and polystyrene-graft copolymer mixtures were added in powdered form to one ply from each test specimen using a homemade column-loading system. This system allowed the delivery of measured amounts of evenly distributed powders onto the test areas. Table I lists the various compositions of the test specimens and the number of the test specimens used in the study.

The test specimens (composed of two plies) were loaded onto aluminum cauls and placed in the press. Each specimen was pressed at 50 psi and 149 \(^\circ\text{C}\) for 3 min. Upon cooling, a band saw was employed to remove 1/2 in. from each end of the specimen (to enable them to fit into the 4 in. grips on the testing machine). A high-speed drill press (12,000 rpm) fitted with a 1/8 in. router bit was then used to cut the cross grooves into each specimen to isolate the glueline for testing. The specimens were conditioned at 21 \(^\circ\text{C}\) and 50% relative humidity for 7 days. Prior to actual testing, a caliper (precision of \(\pm 0.001\) in.) was used to measure the glueline area isolated for testing. The specimens were then inserted into the grips on a Reihle strip shear testing machine and loaded
at a constant rate of 10 lb per sec until failure. The ultimate load at failure and visual estimate of the amount of wood failure were recorded for each sample.

Table I. Composition of the Test Specimens

<table>
<thead>
<tr>
<th>Population</th>
<th>Number of Test Specimens</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>45</td>
<td>Controls, PF resin only</td>
</tr>
<tr>
<td>B</td>
<td>10’</td>
<td>0.02 g of PS only (no resin)</td>
</tr>
<tr>
<td>C</td>
<td>10¹</td>
<td>0.02 g of GP1 only (no resin)</td>
</tr>
<tr>
<td>D</td>
<td>10¹</td>
<td>0.02 g of GP2 only (no resin)</td>
</tr>
<tr>
<td>E</td>
<td>48</td>
<td>PF resin and 0.02 g of PS</td>
</tr>
<tr>
<td>F</td>
<td>45</td>
<td>PF resin and 0.02 g of GP 1</td>
</tr>
<tr>
<td>G</td>
<td>18²</td>
<td>PF resin and 0.02 g of GP 2</td>
</tr>
<tr>
<td>H</td>
<td>46</td>
<td>PF resin and 0.02 g of PS-GP 1 mix³</td>
</tr>
<tr>
<td>I</td>
<td>50</td>
<td>PF resin and 0.04 g of PS-GP 1 mix³</td>
</tr>
<tr>
<td>J</td>
<td>25²</td>
<td>PF resin and 0.02 g of PS-GP 2 mix³</td>
</tr>
</tbody>
</table>

1 In populations B, C, and D, no bonding occurred, and sample fabrication was halted after 10 specimens.
2 The number of test specimens was limited due to insufficient supplies of GP 2.
3 The PS-GrAft Polymer (GP) mixture was made up of 50% by weight of each component.

Synthesis of Tailor Made Cellulose-Polystyrene Graft Copolymers

Problems Encountered. Most of the work done to date in preparation of cellulosic graft polymers has involved free-radical polymerization methods. With these procedures, very few high-molecular-weight molecules were actually grafted as illustrated by low levels of graft substitution [only a small portion of the cellulose substrate was grafted (16,17)]. The molecular weight distribution of the grafted side chains was difficult to control or change, and no knowledge of the nature of the backbone-graft linkage existed. Substantial homopolymer formation occurred; there was poor reproducibility and little control over the grafting process, graft yields, resulting properties, and other features of the graft polymer (18). Clearly, these types of ill-defined and poorly characterized graft polymers with only a few very high molecular weight grafts and low levels of graft substitutions (0.03 to 0.8 polystyryl chains per cellulosic chain and molecular weights ranging from 354,000 to 960,000) would be poor interfacial compatibilizers. In fact, the high molecular weights of the grafts and the low levels of graft substitution would make these materials behave more like blends than graft polymers.
It has been reported that homopolymer blends or random copolymers do not show interfacial activity (19). Therefore, the cellulose graft polymers from free-radical polymerization processes would not be effective compatibilizers. Preferred materials would be precise, well-defined cellulose graft polymers with known backbone-graft linkages developed through procedures that permit variation and control of molecular weight and degree of graft substitution. Higher degrees of substitution than obtained in the free-radical processes would be required.

**New Technology.** As the previous section illustrates, if cellulosic graft polymers are to be employed in adhesive applications, new synthetic approaches must be developed. The new synthetic procedures must allow control of the molecular weight and number of resulting side chain grafts (degree of graft substitution), elimination or drastic reduction of concurrent homopolymer formation, and exercise of direct knowledge and control over the linkage between the cellulosic backbone and the attached side chains.

New synthetic approaches to cellulosic graft polymers have been developed through use of anionic polymerization techniques that allow this to come about (20-24). Thus, the properties of the graft polymers can be tailored by control of parameters such as the molecular weight of the side chain grafts, elimination of concurrent homopolymer formation, the number and type of grafted side chains, knowledge of the linkage between the cellulose backbone and the side chain graft. The method involves: 1) introduction of electrophilic or leaving groups onto the cellulose backbone by chemical modification (i.e., introduction of reactive sites onto the cellulose backbone); 2) preparation of the “living” synthetic polymer of desired molecular weight by anionic polymerization techniques; and 3) reaction of the “living” synthetic polymer with the modified cellulose under homogenous reaction conditions.

Anionic polymerization methods provide an extensive and unprecedented control mechanism over polymerization processes. This includes polymer composition, microstructure, molecular weight and molecular weight distribution, and monomer sequence distribution. This is the key to our approach because we now have the ability to control the essential parameters of the side chain synthetic graft that dictates the properties of the graft polymer. Through regulation of the ratio between the reactive sites on the cellulose backbone and the synthetic polymer anion (the “living” synthetic polymer), the degree of substitution (DS) of the graft can be controlled. The synthetic polymer anion we have used is generally a carbanion (21-23) or a carboxylate anion (24), and the reactive sites on the cellulose backbone are good leaving groups like tosylate (23) and mesylate (24). Thus, the reaction chemistry essentially involves an $S_N2$ type nucleophilic displacement reaction of the tosylate or mesylate group by the synthetic polymer anion. Therefore, there is no uncertainty in the nature of the backbone-graft linkage in our synthetic approach. Concurrent homopolymer formation is eliminated, and any homopolymer formed during the coupling stage is easily extractable.
Thus polystyryl carbanions and polyacrylonitrile carbanions prepared by anionic polymerization were reacted with cellulose acetate or tosylated cellulose acetate in tetrahydrofuran under homogenous reaction conditions. The carbanions displaced the acetate groups or the tosylate groups in a $S_N2$-type nucleophilic displacement reaction to give CA-g-PS and CA-g-PAN. Mild hydrolysis to remove the acetate/tosylate groups furnishes the pure cellulose-g-polystyrene (Figure 3).

Cellulose graft polymers having ester linkages with control over the molecular weight of the side chain graft (24) have also been prepared. In this synthesis, the polystyryl carbanion prepared by anionic polymerization techniques has been modified by capping with carbon dioxide to generate the polystyryl carboxylate anion (1) (Figure 4). While this anion is not sufficiently reactive to displace acetate groups from cellulose acetate, it is, however, sufficiently nucleophilic to displace better leaving groups like the mesylate group from a mesylated cellulose acetate backbone with the concomitant formation of an ester linkage.

A further advantage of the direct use of polystyrene carboxylate anions over polystyryl carbanion is that water does not interfere with the grafting reaction. The reaction is essentially complete at 75 °C after 20 hours. Grafting yields appear to be limited by the efficiency of carboxylation of the polystyrene. We have, for example, prepared a graft polymer product having one polystyryl ester chain of molecular weight 6,200 for every 17 anhydroglucose units of the cellulose backbone. With this approach, monodisperse polystyryl ester chains of any predetermined molecular weight can be grafted onto the cellulose backbone in a consistent manner.

Anionic polymerization of styrene with sodium naphthalene as the initiator gave the difunctional polystyryl carbanion of desired molecular weight that, on reaction with CO$_2$, furnished the polystyryl polystyryldicarboxylate anion (2) (Figure 5). Reaction of this anion with mesylated cellulose acetate resulted in the formation of a solid gel, indicative of crosslinking. Crosslinking is to be expected, since both ends of the polystyrene chain could potentially react with the mesylate groups on the cellulose backbone as shown in Figure 5 (24). We have prepared crosslinked graft polymers with polystyrene of molecular weight 10,000 and one polystyryl crosslink for every 23 anhydroglucose units. These well-defined, tailor-made cellulosic graft polymers prepared by the newly developed anionic polymerization procedures show promise in serving as compatibilizers of interfacial agents for developing new polymer blends of wood, phenolic resins, and polystyrene. A series of relatively simple bonding experiments was designed to support or reject the ability of the new graft polymers to facilitate bonding between wood and plastic materials.

**Bonding Studies**

The potential use of cellulose graft polymers to compatibilize the linking of a natural polymer (wood) with a synthetic polymer (polystyrene) is based on
Figure 3. Grafting of polystyrylcarbanion onto tosylated cellulose acetate. Reprinted with permission from ref. 27. Copyright 1988 Humana Press.
Figure 4. Grafting of polystyrylcarboxylate anion onto mesylated cellulose acetate.
Figure 5. Formation of crosslinked graft copolymer by using polystyryldicarboxylate anion.
the premise that the graft polymer will link the wood and polystyrene through the cellulose and polystyrene phases of the graft polymer, respectively, and not adversely affect the bonding of wood. As previously discussed, the polymer literature documents the use of graft polymers to successfully compatibilize dissimilar synthetic polymers to produce materials with enhanced bond strengths and properties, but this procedure has never been applied to combining wood with plastics.

A set of limited, exploratory investigations was initiated to test the proposed bonding concept with the newly developed graft polymers. Two different graft polymers were selected and prepared for initial observation. They were:

GP 1, Cellulose-g-PS
(MW of PS = 6,250, PS content = 58%)

GP 2, Crosslinked Cellulose-g-PS
(MW of PS = 10,900, PS content = 64%)
The initial research objectives included developing a simple experimental procedure to study how the graft polymers, polystyrene, and a commercial phenol formaldehyde resin interact when combined with wood under heat and pressure. Two-ply lap shear test specimens were used for a comparative test.

All specimens were prepared and tested according to ASTM D 2339-82 (25), with modifications as described in experimental sections. The results are shown in Figure 6. Under the conditions selected for this study, good bonding was achieved with most of the control specimens - population A. The median percent wood failure for the population was 70%. An analysis of the test populations shows support for the premise that the graft polymers have a favorable influence on bond formation when compared to polystyrene alone. Samples containing PF resin and 0.02 grams of polystyrene resulted in an average bond strength of 334 psi (population E), demonstrating the inherent incompatibility of the wood and polystyrene phases. It is also possible that this incompatibility may be between the polar phenol formaldehyde resin and the hydrophobic polystyrene. When the polystyrene was replaced with the same amount (by weight) of one of the two graft polymers, bond strengths increased to 658 and 819 psi, respectively (populations F and G). Thus, when the polystyrene plastic phase is covalently linked to a cellulose backbone, it can be bonded to the wood. Bond strengths for these specimens fell just below those for the control population. However, it must be noted that the cellulose in the graft polymer had very few free hydroxyl groups available for bonding. Hydrolysis of the acetate groups to hydroxyl groups may produce graft polymers capable of even greater bond strengths.

Replacing the 0.02 grams of polystyrene with 0.02 grams of 50:50 mixture (by weight) of polystyrene and one of the graft polymers also led to increases in bond strengths. Samples produced with a PS/GP mixture containing the linear graft polymer yielded an average bond strength of 415 psi (population H), and samples containing a mixture with the crosslinked graft polymer showed an average bond strength of 519 psi (population J).

Additional specimens were prepared with 0.04 grams of the PS/GP 1 mixture (population I). In these specimens, an attempt was made to overload the PF resin with an excess of the powdered materials. This amount of powder completely covered the area under investigation and caused difficulty in assembling the samples. Even under these extreme loading conditions, a bond strength of 446 psi was obtained, which represents a statistically significant increase when compared to the 334 psi bond strength developed in population E.

The results from this study are very encouraging and provide support for continued investigations into the proposed bonding theory. We believe that the bond strengths can be significantly raised from present levels as a number of different parameters that can impact bonding efficiency are adjusted. Simply modifying the manner in which the graft polymer and polystyrene are added to the wood resin matrix may lead to significant increases in bond strengths.
Figure 6. Preliminary bonding test results.
In the completed study, exact amounts of the powdered materials were sprinkled onto the wood-resin surface. Analysis of the test specimens revealed that under the press times and temperatures used the phase transition of the polystyrene side chains on the graft polymer was not efficient. Further, in order for the graft polymer to be effective as an interfacial agent, it must locate preferentially at the blend interface (21). The research team hopes to develop procedures in the future to allow the polystyrene and graft polymers to be dissolved in an organic solvent for application to the wood resin surface. This should allow the graft polymer to locate at the blend interface and improve bonding efficiency.

Results from the initial resin studied are also being employed in the development of additional experimental procedures. Plans are currently being drafted to prepare three-ply test specimens that are similar to the specimens used in the initial study, with the middle ply consisting of solid polystyrene. Comparing specimens with and without the graft polymers introduced to the ply interfaces should provide additional information on the ability of the cellulosic graft polymers to facilitate bonding between wood and plastic materials. If this approach proves successful, additional procedures will then be developed for the production of simple composite specimens.

Statistical Analysis. Each population was compared to all other populations at the 95 and 99% significance levels to determine if a statistical difference was presented between the populations. The test used followed the outline presented in Neter et al. (26). The results of this analysis can be illustrated on a number line. The average bond strength for each population is included, and the bracketed lines group populations that are not statistically different (Figure 7).

Conclusions

This research project represents initial studies into a new approach to blending thermoplastic materials like polystyrene with wood materials, leading to a new class of wood-plastic composites. Traditional wood-plastic composites have involved the impregnation and subsequent in situ polymerization of vinyl monomers. This procedure has been adopted for selected products for which improved physical properties justify increased production costs. While producing mixtures or blends of wood and plastics, these types of composites do not demonstrate significant chemical bonding between the wood and plastic components.

Encouraging results on the bonding of plastics to wood using tailor-made cellulose-polystyrene graft polymers as compatibilizers or interfacial agents may offer a new approach to the engineering of wood-plastic products with improved mechanical and physical properties for a variety of applications. It also holds the potential of opening up new markets for renewable resources in the form of woody materials. For example, polystyrene production is currently $3.9$ billion
Figure 7. Statistical analysis of the bond strengths for the test populations.
lbs per year with a dollar value over 1.6 billion. This material is extensively used in packaging, appliances, housewares, and serviceware. It is conceivable that if the renewable resource materials (especially various byproducts like sawdust, generated by the wood industry) could be blended with polystyrene for processing and fabrication similar to existing styrenic plastics, a completely new market in disposable cups, trays, molded containers, and packaging materials, would be created. Environmental concerns caused by discarding nonbiodegradable plastics should make the "biodegradable," renewable resource-based materials very attractive. The study described here on the blending and bonding of two incompatible polymers (wood and polystyrene) using a novel cellulose graft polymer as the interfacial agent (compatibilizer) presents all of these exciting renewable resource utilization possibilities.

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Literature Cited


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