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EFFECTS OF AZIDOSILANE TREATMENTS OF WOOD AND CELLULOSE FIBER SURFACES ON ADHESION TO POLYPROPYLENE

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ABSTRACT

Wood strip surfaces (Aspen and Birch) and cellulose fibers (Birch, pulped paper fibers) were treated with azidosilane coupling agent, via immersion in methylene chloride and methanol solutions respectively, and then subsequently dried. Polypropylene films were compression molded to the wood surfaces and peel forces were measured. The treated cellulose fibers were suspended and mixed with polypropylene fibers in water, formed into thin sheets by wet forming, dried, and compression molded to melt the polypropylene.

Treated wood surfaces gave two to six times the dry peel force versus untreated wood surfaces. However, the wet peel force of treated wood degraded to that of untreated wood. The elongation, fail stress, and tensile energy absorption of treated molded sheets were all increased over the untreated fibers for both dry and wet testing; the wet-tested properties were especially enhanced by the silane treatment.

INTRODUCTION

Coupling agents have been used to improve the bonding between hydrophilic cellulosic materials and hydrophobic polyolefins.[1] We are currently studying the effects of coupling agents on the bonding in wood-polyolefin composites. One coupling agent for this system is azidosilane which can form covalent bonds with both cellulosics and polyolefins. Azidosilane has the structure:

$$N_3SO_2\text{-}R\text{-}Si(OR')_3.$$

Bonding to cellulosics is through the formation of siloxane bonds, while bonding to polyolefins is through the formation of sulfonamide bonds[2].

This paper discusses the results of studies of azidosilane coupling agent with wood veneer-polypropylene laminates and with cellulosic fiber-polypropylene papers. For the veneer samples the force required to peel the polypropylene film off the veneer was measured, while in the paper samples the tensile strength, tensile modulus, elongation and tensile energy absorption were measured.

EXPERIMENTAL

The study of azidosilane as a coupling agent for cellulosic-polypropylene systems consisted of three distinct experiments. The first (Experiment A) was an initial study of the proesssing variables on azidosilane treated wood veneer-polypropylene laminates. The second (Experiment B) was a study of the water durability of azidosilane treated wood veneer-polypropylene laminates. The response measured in the first two experiments was 90° peel force. The third (Experiment C) was a study of the wet and dry tensile properties of treated birch fiber-polypropylene fiber paper.

Materials

The polypropylene used in Experiments A and B was Soltex Fortilene 9101 homopolymer spheres with a density of 0.900 g/mL and a melt flow index of 2.5 g/10 min (23°c/2160g). The polypropylene used in Experiment C was Hercules Pulpex P Ad-V fibers with a density of 0.900 g/mL, an average fiber length of 1 mm and an average fiber diameter of 30 microns. The coupling agent used was Hercules AZ-CUP. The cellulosic materials were Quaking Aspen (Populus tremuloides) and Yellow Birch (Betula alleghaniensis) knife-cut veneers and unbleached, refined (to 570 ml CSF) Kraft fibers from Yellow Birch.

Coupling Agent Treatment

The azidosilane-treated veneer sheets (Experiments A and B) were silanated to approximately 50% monolayer coverage in a solution of methylene chloride and then vacuum-oven dried at 70°C. The untreated veneer sheets were wet with pure methylene chloride and then vacuum-oven dried. The azidosilane-treated birch fiber (Experiment C) was dry fiberized in a Waring blender and then treated to approximately 100% monolayer coverage in a solution of methanol. The untreated fiber was not dry fiberized in the blender or exposed to methanol. No significant change in the fiber length was seen after the dry fiberization step.

Veneer Samples

Experiment A

Veneer sheets (175 by 175 by 3 mm) were prepared as described above and then a polypropylene film was compression molded onto each sheet at 175°C. A systematic study of the laminated veneers was performed in a replicated full factorial experiment[3]. The variables studied were: molding pressure (0.14 and 0.28 MPa), molding time (3 and 6 minutes), veneer species (Quaking Aspen and Yellow Birch), and coupling agent (none and azidosilane).

The polypropylene film was prepared by extruding through a slit die at 180°C and calendering to 2 mm thickness. Each laminated veneer sheet was cut into six strips (175 by 25 by 3 mm) parallel to the wood grain for peel force measurement. The 90° peel force was measured continuously along the length of each strip, using an Ametek universal testing machine at a peel rate of 100 mm/min. A mean peel force for each sheet was obtained by averaging the peel force over the middle 100 mm of all strips.

Experiment B

The water durability of the laminated veneer samples was evaluated in a second replicated full factorial study. In this study the variables were: veneer species (Quaking Aspen and Yellow Birch), coupling agent (none and azidosilane) and water soak (none and 24 hours). The veneer sheets were prepared as above, and a polypropylene film was compression molded onto each sheet at 175°C, 3 minutes and 0.14 MPa. Half the samples were then submerged 25°C distilled water for 24 hours and redried in a vacuum oven at 70°C. The Peel force was measured as in Experiment A.

Fiber Samples

Experiment C

The birch fiber-polypropylene papers were prepared by mixing 75% birch fiber and 25% polypropylene fiber in water to form a slurry. This slurry was then drained through a stainless steel mesh to form a 300 by 300 mm wet paper sheet. The sheets were dried to approximately 50% water content by pressing between sheets of blotter paper at 25°C and 0.76 MPa for 30 seconds. To prevent blow out during melt processing, the paper sheets were dried by pressing between stainless steel platens, at 135°C and 0.69 MPa, for 1 minute. The 300 by 300 mm sheets were then cut into four 150 by 150 mm sheets which were compression molded, at 190°C and 2.4 MPa, for 3 minutes to melt the polypropylene. The resulting sheets were approximately 0.2 mm thick. Teflon platens were used to avoid release agents. These molding conditions were obtained from extensive studies with regard to molding time, pressure and temperature.[4,5,6,7] Deviations from the conditions used above gave poorer performance, but the general conclusions are the same.

Strips 150 by 13 mm were then cut from the sheets and conditioned for wet and dry tensile testing. The dry samples were conditioned for 24 hours at 23°C and 50% relative humidity, and the wet samples were soaked in water for 24 hours at 23°C. The dry samples were tested at 50% relative humidity and the wet samples were tested wet. The testing was done on an Instron (model 4201) at a constant strain rate of 3 mm/minute.

RESULTS AND DISCUSSION

Veneer Samples

The results of Experiment A are summarized in Table I and Figure 1. Table I shows the main effects of each of the variables studied. We note that all four variables showed significant effects at 95% confidence level. with molding time and coupling agent having the largest effects. Figure 1 illus- trates the most important features of the azidosilane treated system. First, the responses of the two veneer species were very similar. Second, the mold- ing time had only a small effect on untreated samples. Third, azidosilane treatment increases the peel force by approximately 100% at short molding times and approximately 250% at long molding times.

These results indicate that azidosilane is an effective coupling agent for the wood-polypropylene system. The significant increase in peel force for azidosilanated samples at long times is consistent with the activation of azide groups at this temperature.[2]

Table I
Experiment A: Main Effects on Dry Peel Force

Variable	Level	Peel Force[a]	Effect[b]
Molding Pressure	0.14 MPa	3.43 N	-
	0.28 MPa	3.96 N	15%
Molding Time	3 min	2.58 N	-
	6 min	4.81 N	86%
Coupling Agent	None	1.92 N	-
	Azidosilane	5.47 N	185%
Veneer Species	Birch	3.46 N	-
	Aspen	3.94 N	14%

a Response averaged over all other variables.
b Percent change from lower level.

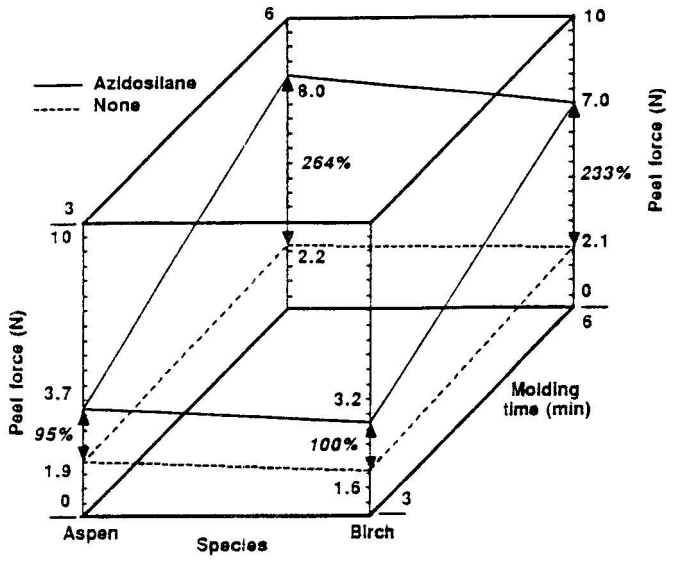

Figure 1: Peel force as a function of veneer species, pressing time and treatment with azidosilane. Experiment A. (All data points averaged over 0.14 and 0.28 Pa molding pressures. Percentage figures on axes represent the increase above the untreated samples.)

The effects of water soaking on peel force (Experiment B) are summarized. in Figure 2. Again we note the important features of the system. First, the response of the two veneer species are very similar. Second, the azidosilane treatment does not improve the water durability of the system. When these results are considered with the results from experiment A, we conclude that a higher degree of coverage may be required to form the silane network required for water durability. The network requirement for silane water durability has been discussed by Plueddemann.[8]

Paper Samples

The results of Experiment C are summarized in Table II and Figure 3. In Table II we note that the azidosilane-treated samples exhibited higher tensile strength under both the wet and dry conditions. When compared to untreated samples, azidosilane-treated samples showed the following improvements: an increase of 22% in dry tensile strength, an increase of 220% in wet tensile strength, an increase of 12% in dry elongation, an increase of 158% in wet elongation, an increase of 31% in dry tensile energy of absorption and an increase of 633% in wet tensile energy of absorption. Figure 3 shows an obvious improvement in both elongation and tensile strength for the wet tested azidosilanated samples. The improved wet strength of the treated papers, in contrast to the poor wet veneer peel force, suggests that complete surface coverage with azidosilane will improve the water durability.

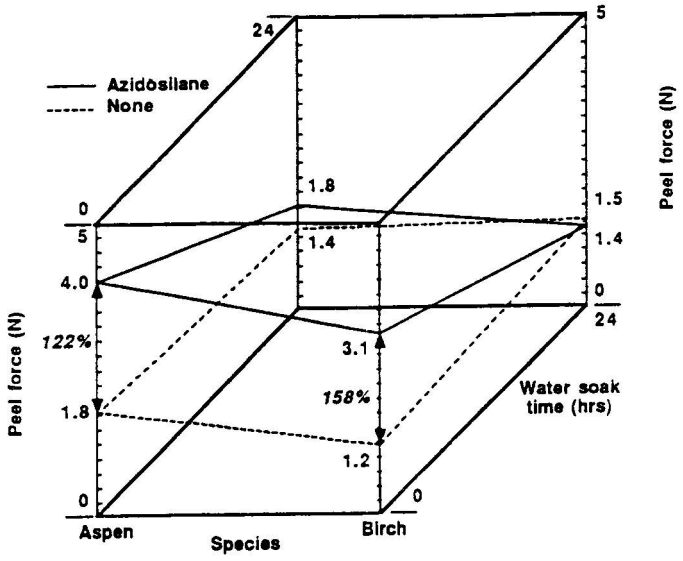

Figure 2: Peel force as a function of veneer species, water soak and treatment with azidosilane. Experiment B. (Percentage figures on axes represent the increase above the untreated samples.)

Table II
Tensile Properties of Birch-Polypropylene Papers: Experiment C[a]

Sample	Condition	Tensile Strength (MPa)	Elongation (%)	Tensile Modulus (GPa)	TEA[b] kJ/m^2
Untreated	Dry[c]	53.8	1.6	5.59	31.5
	Wet[d]	9.5	2.6	0.72	8.4
Azidosilanated	Dry	65.4	1.8	3.86	41.2
	Wet	30.4	6.7	0.96	61.6

a Molding conditions: 3 min, 2.4 MPa and 190°C. Tested at 3 mm/min elongation rate.
b Tensile Energy Absorption = area under stress-strain curve.
c Conditioned and tested at 23°C, 50% relative humidity.
d Water soaked 24 hours and tested at 23°C. 100% relative humidity.

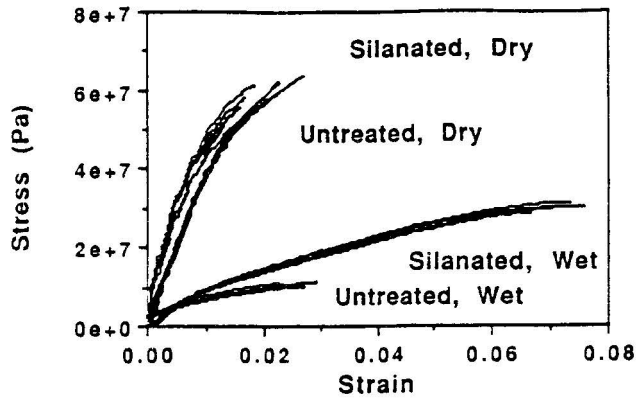

Figure 3: Stress-strain curves for treated and untreated birch fiber-polypropylene paper, wet and dry conditioned. Experiment C.

CONCLUSIONS

The results of this study indicate that azidosilane can be an effective coupling agent for cellulosic/polyolefin systems. The poor water durability of azidosilanated veneer, in contrast to the paper. indicates the need for further study of azidosilane concentration effects and network formation on wood substrates. We are currently pursuing these aspects.

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