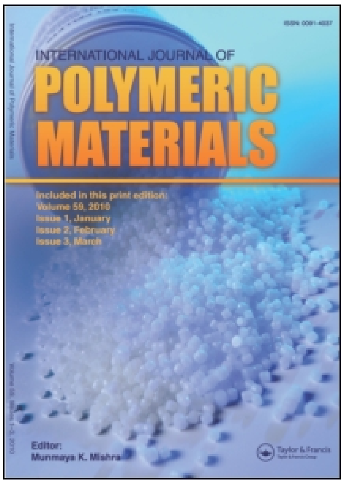

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Cellulose/Polypropylene Composites: The Use of AKD and ASA Sizes as Compatibilizers

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Cellulose/Polypropylene Composites: The Use of AKD and ASA Sizes as Compatibilizers

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Alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA) were used in both solution and emulsion forms to treat 100% cellulose and 70/30 wt.% cellulose/polypropylene composite sheets made by both an air-formation technique and traditional wet handsheet formation. In all cases, the air-formed sheets had poorer mechanical properties than did the handsheets. While the treatments appeared to have a visible affect on the spreading of polypropylene over cellulose, the effects of the treatments on mechanical properties were almost always negative. Annealing the wet-formed handsheets for five minutes at 130°C before pressing gave control sheets with improved modulus, strain-to-break, and burst strength, but had a slight negative effect on air-formed sheet properties. The effect of treatments on the water durability of the air-formed sheets was minimal or adverse, while for the wet-laid handsheets, the treatments were slightly beneficial if the sheets had been annealed, but detrimental if they had not.

KEY WORDS Composite, alkyl ketene dimer, alkenyl succinic anhydride, compatibility, mechanical properties, water durability.

INTRODUCTION

It has been widely noted that a key to good composite properties lies in compatibility between matrix and filler. In the wood fiber-polyolefin system, the highly polar nature of the cellulosic surface does not lend itself to strong interactions with the non-polar polymer. Modification of the cellulose surface, either by chemical coupling agents or grafting, has proven to be beneficial in improving the strength and modulus, as well as the water resistance of these composites.[1-9]

In the realm of paper manufacturing, sizing agents are one of the most widely used methods of changing the hydrophilic nature of cellulose. In particular, alkyl ketene dimer (AKD) and alkenyl succinic anhydride (ASA), shown in Figure 1, are two of the most common sizes used in alkaline papermaking.[10,11] The intriguing feature of these sizes is the dual polarity of their structure: a polar component to react with the cellulose surface and a nonpolar (hydrophobic) component which should be compatible with polyolefins.

The purpose of this study was to discover what effect treatment of cellulose pulp with AKD and ASA, in both solution and emulsion form, had on the mechanical properties of cellulose and polypropylene composite sheets made by both air-forming and conventional wet handsheet forming.

EXPERIMENTAL

A) Materials

Bleached kraft cellulose pulp in dry-lap form (Ultranier-J) was obtained from ITT Rayonier. Before use, the pulp was slurried, dewatered, and fiberized (Bauer single-disk mill refiner, 3600 rpm, .01 cm disk separation).

The polypropylene used was Hercules Pulpex P AD-H, which contains a surface treatment of <1.0 wt.% poly(vinyl alcohol) for better water dispersibility.

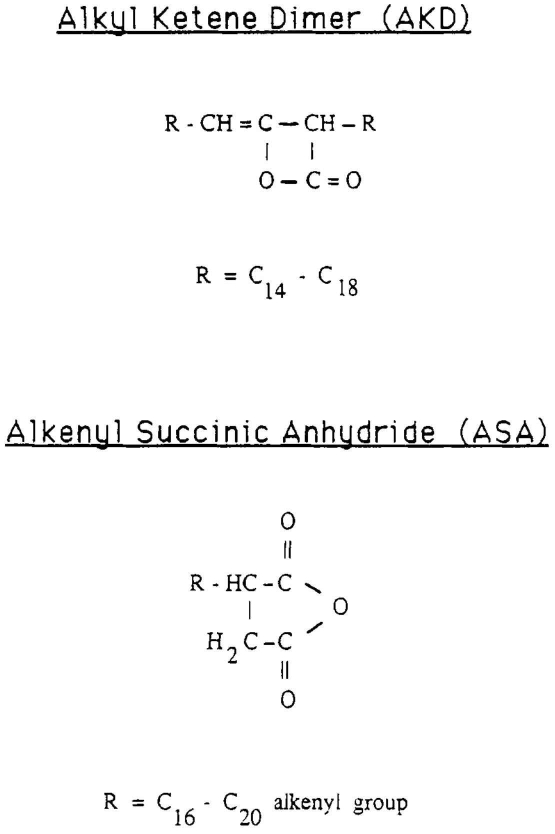
Hercon 70 (Hercules) AKD emulsion was diluted to prepare the AKD emulsions used in the study. Aquapel 364, a dry AKD wax, also provided by Hercules, was used in all AKD/toluene solutions.

ASA/toluene solutions were made using ACCOSIZE 18 (American Cyanamid) synthetic size, while ASA emulsions were produced with ACCOSIZE 18 and ACCOSIZE 72 cationic starch (1:3 starch) as an emulsifier dissolved in water.

B) Air-formation

Figure 2 shows a schematic of the forming apparatus used to make the air-laid sheets.[12] Sheets were either 100% cellulose fiber or 70/30 (wt.%) cellulose/polypropylene. Enough fiber for one 205 g/m^2 sheet (plus about 10% extra to compensate for "lost" fiber) was added to the top agitation chamber. A vacuum of 7–10 kPa was applied to the plenum at the bottom. Air-jets into the agitation chamber were alternately pressurized by 500 kPa compressed air, forcing the fibers through an 8 mesh screen and down through the tower. The fibers collected on the forming screen at the bottom of the tower, creating a web of fibers. This web can be easily removed and pressed into a sheet.

For composite sheets containing polypropylene, static and clumping proved to be a problem at times in the formation process. To help break apart any polypropylene clumps prior to sheet air-formation, it was run through an FPL-designed



Alkyl Ketene Dimer (AKD)

$R = C_{14} - C_{18}$

Alkenyl Succinic Anhydride (ASA)

$R = C_{16} - C_{20}$ alkenyl group

FIGURE 1 Chemical structures of ASA and AKD.

"Nit-Separator," as represented in Figure 3.[12] The "accepts" that passed through the 16 mesh separator screen were next mixed with water in a Waring blender to eliminate static surface charge. The fiber was dried before use.

C) Wet-laid Handsheet Formation

Prior to handsheet formation, the cellulose pulp was beaten (Valley) to approximately 500 Canadian Standard Freeness. This was necessary since unbeaten pulp does not form homogeneous handsheets. For all sheets, the fibers were mixed in a bucket with water and allowed to soak overnight before sheet formation. Handsheets were formed by Tappi method T205 am-88,[13] but with tap water substituted for deionized water. Tap water has been found to increase the rate of AKD reaction.[14]

D) Treatment Methods

AKD and ASA treatments were applied differently for the air-formed sheets vs. the wet-formed handsheets. Cellulose fiber used for the air-formed sheets was treated prior to sheet formation at a 1.5 wt.% (by cellulose fiber weight) level.

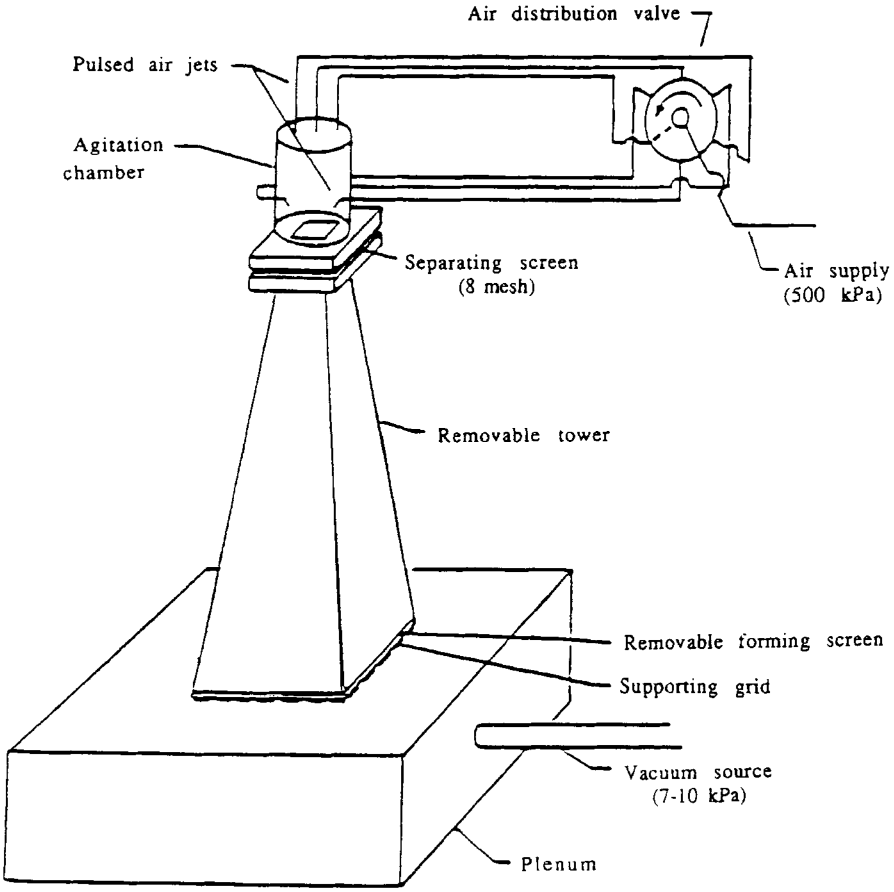


FIGURE 2 Schematic diagram of air-forming apparatus.

This treatment level should be more than adequate to ensure complete reaction.[15,16] In fact, excess unreacted AKD has been shown[15] to contribute to the sizing process. Solution treatments were prepared by dissolving the required amount of AKD or ASA in toluene at 0.1% concentration. AKD emulsions were prepared by diluting a commercially available AKD emulsion (Hercon 70, Hercules) with water to the same concentration. ASA emulsions were prepared by dissolving a starch (ACCOSIZE 72 cationic starch, American Cyanamid) in water with a Waring blender and then forming an emulsion by adding ASA (1:3 starch). Each treatment was prepared and poured over batches of 30–35 oven-dry (O.D.) grams of fiber and stirred for two minutes. The excess liquid was drained off using a Buchner funnel and the resulting fiber was broken apart by hand into a large pan and dried in a 105°C convection oven for one hour.

In the case of handsheets, ring-dried handsheets were subjected to each treatment for five minutes (1.5 wt.% of cellulose fiber). Sheets were then allowed to air-dry in a laboratory hood for 30 minutes, followed by one hour in a 105°C convection oven.

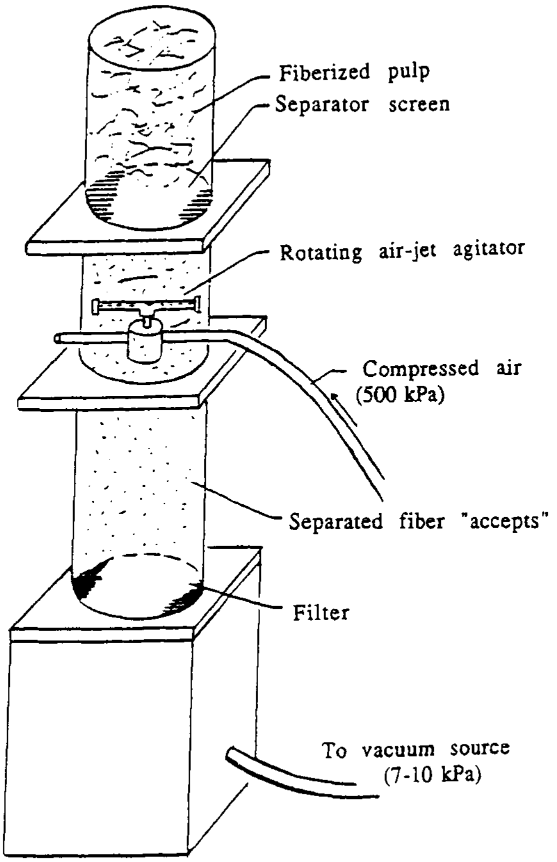


FIGURE 3 Schematic diagram of FPL-Designed "Nit-Separator."

E) Sheet Annealing

Some of the wet-formed handsheets and air-formed sheets produced and treated as above underwent an additional thermal treatment step. Prior to pressing, the sheets were placed in a circulating oven for five minutes at 130°C. Sheets were then pressed as described below. The intended purpose of this step was to make the high-energy poly(vinyl alcohol) surface treatment on the polypropylene invert and yield a lower-energy polypropylene surface.

F) Sheet Pressing

Prior to pressing the 100% cellulose air-formed sheets, they were placed in a humidity room (90% RH) for at least 96 hours to increase the moisture content of the fibers in hopes of increasing the amount of hydrogen bonding in the sheets. No other sheets underwent this step.

All handsheets and air-formed webs were placed between two thin 22.9 x 22.9 cm stainless steel plates covered with a thin Teflon film and pressed in a Carver laboratory press at approximately 172°C and 350 psi (2260 kPa) for two minutes.

Upon removal from the press, the sample and molding plates were sandwiched between a 2.5 cm steel block (bottom) and another (ca. 1 kg) steel plate (top) for two minutes to help prevent wrinkling in the sheets. After pressing, sheets were preconditioned in a controlled room (30 ± 5°C, 25 ± 10% RH) for at least 24 hours before being moved to a conditioning room (23 ± 1°C, 50 ± 2% RH) where they remained for at least 24 hours before testing.

Sheets used for 48 hour-soak samples did not undergo the preconditioning/conditioning step, but were submerged in approximately 2 to 3 cm of distilled water for 48 hours. Samples were then removed, blotted, and tested wet to evaluate the water durability of the sheets.

G) Mechanical and Physical Tests

Burst testing was done using a Mullen Tester Model CA (Perkins & Son, Inc.). Reported data are the averages of eight to ten samples.

A Taber V-5 Stiffness Tester was used in measuring sheet stiffness. Fourteen to sixteen samples were measured for each data point.

Internal bond measurements were done slightly differently than Tappi method T541 pm-83.[13] Instead of pressure-sensitive tape, heat-sensitive film (MT5 permanent Dry Mounting Tissue, Seal, Inc.) was used. Samples size was 4.45 × 4.45 cm (with test area of 5.07 cm^2). Film bonding was done at 120°C for 45 minutes. Specimens were tested on an Instron Tester (Model TTCM) at 0.2 cm/min. crosshead speed. Data are the average of 27–30 samples.

Other mechanical properties (tensile modulus, tensile strength, elongation-at-break, tensile energy absorption) were measured using necked-down (dog-bone) specimens and an Instron Tester (Model 4201). The crosshead speed was 3 mm/min. Properties were calculated by a regression program, unless otherwise stated, with reported data the average of fourteen to sixteen samples.

Density calculations were done by measuring the weight and average thickness of 7.62 × 7.62 cm or 10.16 × 10.16 cm samples. Thicknesses were measured using an effective thickness micrometer, described elsewhere.[17] Values reported are the average of five measurements.

RESULTS

Figures 4 through 7 summarize results obtained from tensile test measurements and Tables I and II give other testing results.

Dry Properties

As can be noticed, properties of air-formed sheets are in all cases significantly less than those of the handsheets. Also, AKD and ASA treatments nearly always had a detrimental or only slight positive effect on properties if the sheets had not been annealed. Annealing the wet-formed handsheets increased modulus, strain-to-break,

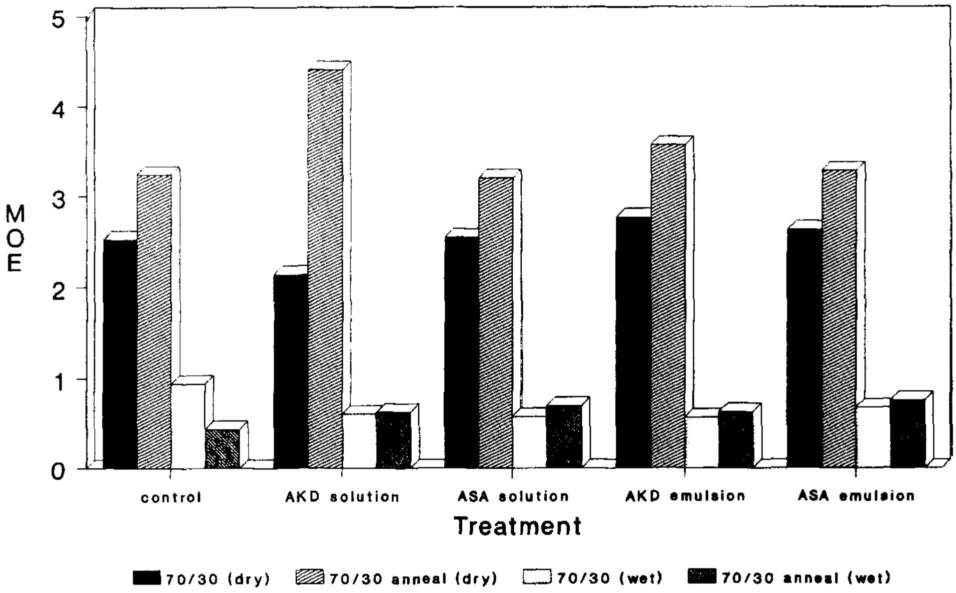


FIGURE 4 Tensile modulus of composite handsheets.

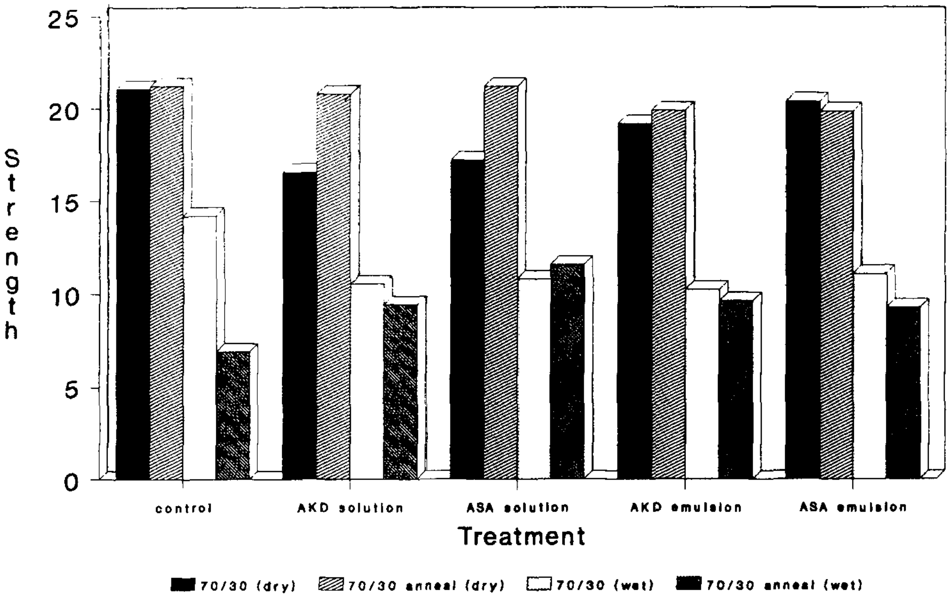


FIGURE 5 Tensile strength of composite handsheets.

and burst strength, but had little positive effect on other dry sheet properties. For air-formed sheets, annealing seems to have a minimal to negative effect on sheet properties.

For 70/30 composite air-formed sheet that were not annealed before pressing, the relatively low density (compared to handsheets) was little effected by the change

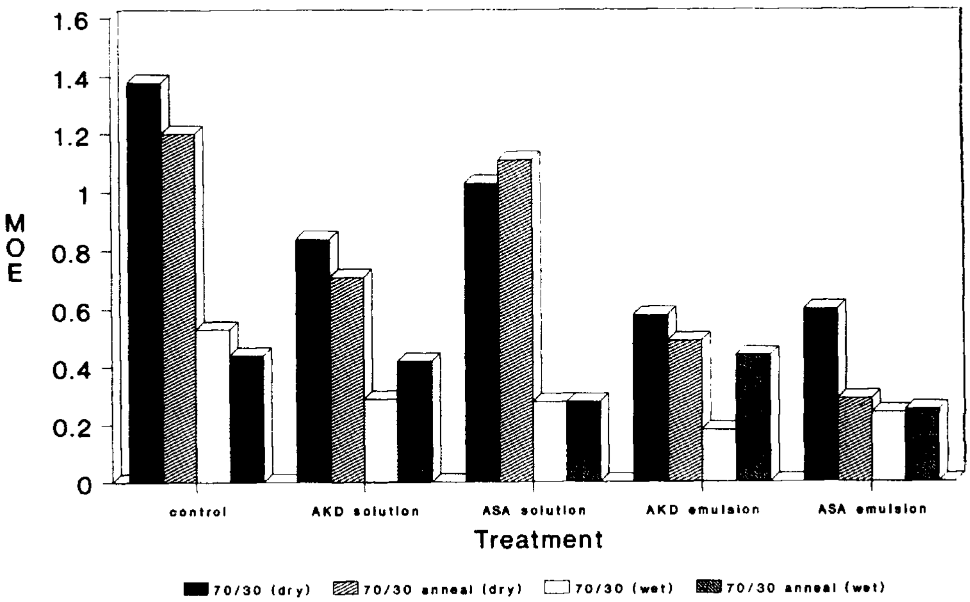


FIGURE 6 Tensile modulus of air-formed sheets.

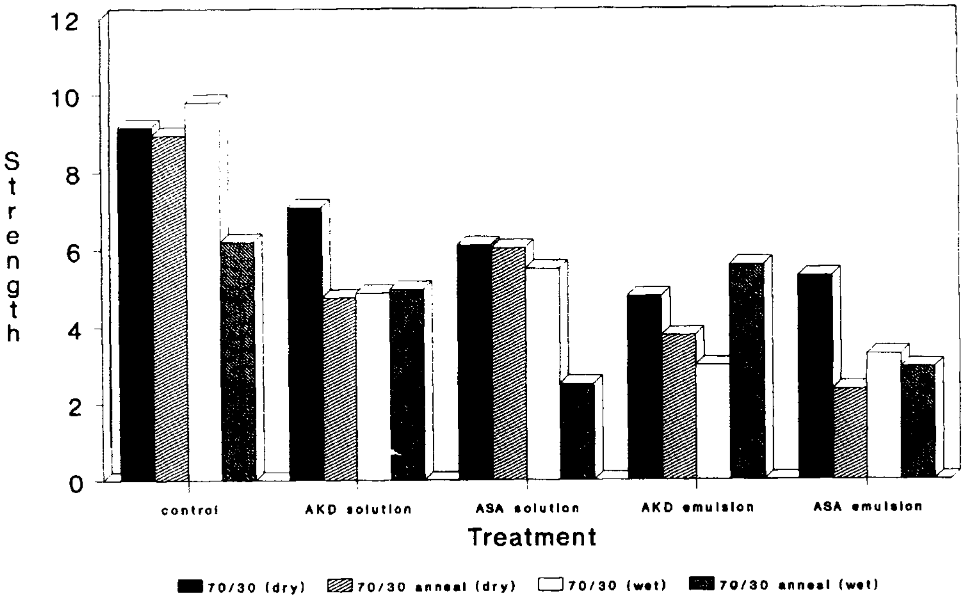


FIGURE 7 Tensile strength of air-formed sheets.

in fiber surface character, but sheets made that included the annealing step show a decrease in density if treated. Wet-formed composite handsheets showed a 4–11% decrease if they were not annealed before pressing, while a slight increase was seen for annealed sheets.

TABLE I

Summary of data for wet-laid handsheets

	Stiffness (g-cm)	Burst Strength (kPa)	Internal Bond (MPa)	Density (g/cm3)	Emax (%)	TEA (MPa)
100 (dry)						
control	24.6 (1.0)	338.5 (19.3)	0.80 (0.10)	0.68	3.82 (0.76)	0.59 (0.13)
AKD solution	28.9 (2.0)	350.3 (17.2)	0.73 (0.04)	0.63	3.74 (0.50)	0.53 (0.09)
ASA solution	29.5 (3.7)	477.1 (42.7)	0.68 (0.05)	0.64	4.20 (0.43)	0.67 (0.09)
AKD emulsion	19.9 (3.3)	337.2 (45.5)	0.32 (0.05)	0.60	4.35 (0.73)	0.45 (0.10)
ASA emulsion	22.2 (5.4)	395.1 (70.3)	0.40 (0.03)	0.63	4.46 (0.66)	0.50 (0.10)
70/30 (dry)						
control	17.7 (1.7)	355.1 (112.4)	1.50 (0.16)	0.81	2.66 (0.59)	0.42 (0.14)
AKD solution	21.7 (2.0)	298.6 (48.3)	1.26 (0.21)	0.72	2.68 (0.78)	0.34 (0.14)
ASA solution	26.4 (4.8)	364.7 (79.3)	1.29 (0.15)	0.73	2.53 (0.92)	0.34 (0.15)
AKD emulsion	23.8 (2.5)	436.5 (68.3)	1.07 (0.17)	0.77	3.68 (0.92)	0.56 (0.17)
ASA emulsion	23.0 (3.4)	514.4 (91.7)	1.17 (0.17)	0.78	4.58 (1.07)	0.74 (0.22)
70/30 (48 hr. soak)						
control	4.1 (1.0)	331.6 (63.4)			7.40 (0.82)	0.66 (0.14)
AKD solution	4.5 (0.7)	291.0 (38.6)			8.28 (1.39)	0.55 (0.20)
ASA solution	4.2 (0.8)	396.6 (83.4)			8.00 (0.85)	0.54 (0.11)
AKD emulsion	4.5 (0.5)	334.4 (73.8)			8.71 (0.85)	0.55 (0.12)
ASA emulsion	3.7 (0.6)	294.4 (41.4)			8.30 (1.08)	0.56 (0.11)
70/30 anneal (dry)						
control	21.9 (3.4)	439.9 (76.5)	1.31 (0.18)	0.69	4.38 (0.65)	0.74 (0.16)
AKD solution	27.2 (3.7)	475.1 (70.3)	1.35 (0.15)	0.70	3.47 (0.76)	0.58 (0.18)
ASA solution	26.5 (4.5)	526.8 (54.5)	1.25 (1.08)	0.73	4.56 (0.76)	0.76 (0.18)
AKD emulsion	23.2 (2.5)	471.6 (88.3)	1.08 (0.21)	0.71	4.78 (0.56)	0.76 (0.12)
ASA emulsion	23.3 (2.8)	569.5 (76.5)	1.15 (0.10)	0.72	4.72 (0.83)	0.75 (0.19)
70/30 anneal (48 hr. soak)						
control	3.9 (0.5)	251.0 (52.4)			6.90 (0.87)	0.30 (0.06)
AKD solution	4.4 (0.8)	266.1 (47.6)			7.34 (1.01)	0.43 (0.09)
ASA solution	4.4 (0.7)	341.3 (76.5)			8.14 (0.68)	0.58 (0.08)
AKD emulsion	4.1 (0.9)	327.5 (51.7)			7.86 (0.86)	0.45 (0.10)
ASA emulsion	3.9 (0.8)	291.7 (61.4)			7.80 (1.00)	0.45 (0.10)

(Standard deviation)

TEA = tensile energy absorption

Emax = strain at break

TABLE II

Summary of data for air-formed sheets

	Stiffness (g·cm)	Burst Strength (kPa)	Internal Bond (MPa)	Density (g/cm3)	Emax (%)	TEA (MPa)
100 (dry)						
control	4.5 (0.9)	23.4 (5.5)	0.15 (0.11)	0.72	0.34 (0.09)	.0051 (.0024)
AKD solution	0.4 (0.3)	--*	0.005 (0.001)	0.48	1.17 (0.49)	.0015 (.0009)**
ASA solution	1.0 (0.6)	--	0.006 (0.004)	0.60	1.02 (0.52)	.0027 (.0012)
AKD emulsion	0.3 (0.1)	--	0.004 (0.007)	0.57	--*	
ASA emulsion	0.6 (0.4)	--	0.03 (0.03)	0.62	1.08 (0.61)	.0017 (.0012)**
70/30 (dry)						
control	7.6 (1.7)	158.6 (48.3)	1.11 (0.4)	0.66	4.88 (2.05)	0.40 (0.23)
AKD solution	5.5 (1.5)	166.2 (33.8)	0.84 (0.3)	0.66	4.52 (1.57)	0.27 (0.16)
ASA solution	7.1 (1.9)	222.7 (59.3)	0.62 (0.2)	0.66	4.05 (1.03)	0.20 (0.08)
AKD emulsion	3.3 (1.1)	77.9 (17.9)	0.04 (0.02)	0.53	3.41 (0.88)	0.13 (0.05)
ASA emulsion	3.7 (1.0)	95.8 (36.5)	0.08 (0.04)	0.61	3.13 (1.02)	0.12 (0.06)
70/30 (48 hr. soak)						
control	2.9 (0.7)	272.4 (63.4)			9.69 (0.42)	0.65 (0.12)
AKD solution	3.4 (1.2)	142.0 (51.0)			8.53 (1.65)	0.30 (0.07)
ASA solution	3.1 (0.8)	189.6 (90.3)			9.26 (0.90)	0.36 (0.10)
AKD emulsion	2.0 (0.6)	93.1 (31.7)			5.67 (2.04)	0.13 (0.08)
ASA emulsion	1.6 (0.6)	90.3 (31.7)			4.64 (1.74)	0.11 (0.05)
70/30 anneal (dry)						
control	13.9 (2.5)	232.4 (46.2)	0.56 (0.22)	0.61	5.45 (1.13)	0.41 (0.12)
AKD solution	12.0 (2.5)	126.2 (20.0)	0.17 (0.09)	0.51	4.39 (1.45)	0.17 (0.06)
ASA solution	16.4 (3.8)	163.4 (40.7)	0.44 (0.21)	0.58	3.39 (1.42)	0.16 (0.08)
AKD emulsion	3.2 (1.2)	63.4 (11.7)	0.06 (0.03)	0.55	2.88 (0.62)	0.08 (0.03)
ASA emulsion	3.4 (1.3)	44.1 (15.9)	0.07 (0.02)	0.51	2.23 (0.60)	0.04 (0.02)
70/30 anneal (48 hr.soak)						
control	2.4 (0.4)	213.1 (65.5)			8.51 ( )#	0.37 (0.09)
AKD solution	3.3 (0.8)	151.7 (46.2)			7.94 ( )#	0.29 (0.08)
ASA solution	3.9 (1.0)	196.5 (62.1)			3.23 (1.02)	0.06 (0.03)
AKD emulsion	1.6 (0.5)	53.8 (21.4)			7.68 ( )#	0.31 (0.10)
ASA emulsion	1.7 (0.6)	51.0 (14.5)			4.51 (1.97)	0.10 (0.06)

(Standard deviation)
* Too low to measure
** Estimated from tensile curves
\# Maxed-out strain gauge on several samples
Actual value is probably higher than reported

TEA = tensile energy absorption
Emax = strain at break

Water-Soaked Properties

The wet strength tensile properties (modulus and strength) of unannealed treated composite sheets, either wet-laid or air-formed, generally showed a greater percentage of decline than did those for untreated control sheets, while other sheet properties tended to show equal declines. For wet-laid handsheets, this trend is reversed if the sheets underwent the thermal annealing step before pressing. Here mechanical properties of treated sheets retain a greater percentage of their original value than do untreated sheets.

For the air-formed sheets, annealing seems to be slightly beneficial, but properties are not dramatically different than annealed control values.

Because of specimen preparation methods, internal bond testing could not be performed on water-soaked samples.

Emulsion vs. Solution

For the air-formed sheets, either of the emulsion treatments gave much poorer sheet properties than did the solution treatments. In the case of wet-formed handsheets, the difference between emulsion and solution treatments appears to be minimal, although solution treatment may give slightly better properties in 70/30 annealed sheets, while emulsion treatment being better in 70/30 unannealed sheets.

DISCUSSION

It is apparent that the effects of AKD and ASA treatments on the adhesion of polypropylene to cellulose are generally not positive. As the sheet densities seem to show, the treatments appear to prevent or decrease intimate contact between the polypropylene-cellulose or cellulose-cellulose fibers unless the sheets (wet-laid) were annealed before pressing.

As might be expected, the air-formed, 100% cellulose sheet, showed the largest effect of the treatments. These sheets are held together mainly by hydrogen bonding between "dry" fibers. AKD and ASA treatment covered the hydrophilic cellulose surface with hydrophobic molecules prior to web formation, reducing hydrogen bonding in the sheet to almost zero. Treatments were less destructive in the wet-formed 100% cellulose handsheets, which had hydrogen bonding established through the formation and drying sequence prior to treatments. As a result, the fibers in these sheets had numerous areas of interfiber bonding that remained intact and untreated.

Visual inspection of the pressed handsheets revealed a rather startling result. Unannealed untreated pressed composite handsheets appeared to have polypropylene-rich segregated areas. But in handsheets that underwent a treatment or annealing before pressing, these areas seemed to be eliminated, as can be seen in Figure 8. This suggests that the treatments (or annealing) had the effect of compatibilizing the surface energies of the two components, facilitating spreading of the molten polypropylene. This appears to be offset by the loss in hydrogen bonding (which provides a significant portion of the strength) between cellulose fibers with hydrophobic surfaces. Thus an overall decline in mechanical properties is observed.

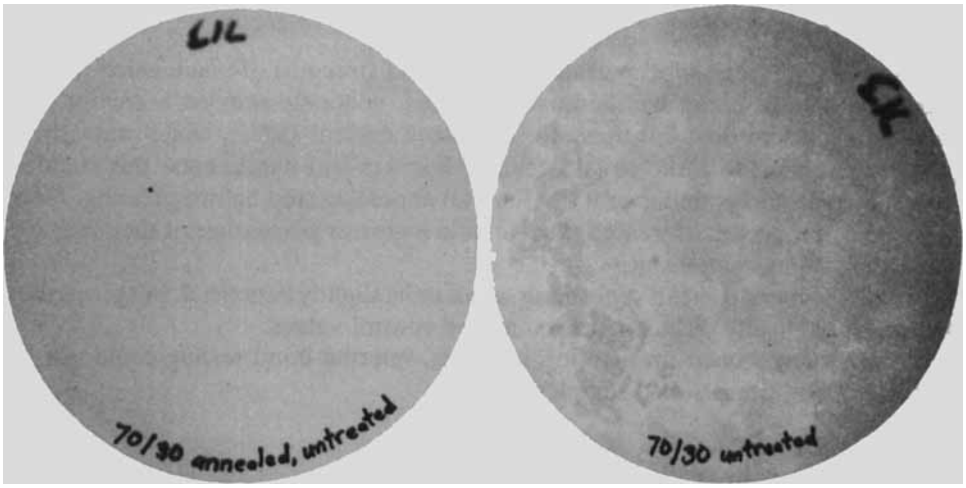


FIGURE 8 Photo of formation differences between untreated annealed and untreated unannealed composite handsheets.

A probable explanation for the poor properties seen in the emulsion-treated air-formed sheets is the inhomogeneity of the pressed sheets. After the cellulose fiber is treated, drying in the oven results in the formation of fiber clumps. While passing through the air-forming apparatus, many of these clumps do not break apart, resulting in poor sheet quality.

Effects of Annealing

It was found during a simple water-submersion test of the polypropylene that heating the polypropylene at 130°C for five minutes noticeably increased the submersion time, while heating at 105°C for up to one hour did not. ESCA analysis of the polypropylene fibers before and after the 130°C heating revealed an increase by nearly a factor of three in the amount of surface oxygen after heating. This corresponds with thermal oxidation of the polypropylene, which has been shown[18,19] to produce various products on the polymer, such as ketones, esters, and acids. This increase in the polar nature of the polypropylene surface is possibly responsible for the increased properties of the annealed handsheets.

The fairly small hydrocarbon chain length ($R = C_{12}\text{–}C_{18}$) of the AKD and ASA treatments, although efficient at changing the hydrophilic nature of the cellulose surface, may not be long enough to be truly incorporated into the polypropylene, resulting in poor adhesion between the two components. Other studies involving maleated polypropylene[4,5,20] a compound strikingly similar to ASA but with a longer chain, have shown it to be an effective coupling agent for wood-polypropylene composites.

CONCLUSIONS

Air-forming composite sheets instead of traditional wet handsheet formation does not provide any additional benefits to the mechanical properties of the sheets, and in fact yields poorer quality sheets. AKD and ASA, in either emulsion or solution form, have little beneficial effect on the mechanical properties of both dry-tested air-formed sheets and dry-tested wet-formed handsheets. Annealing the wet-laid handsheets prior to pressing increases properties over unannealed handsheets, but treatments still have little effect on dry-tested properties. For air-formed sheets, annealed and unannealed sheets are nearly identical in both wet and dry tests. While sheet treatments and annealing do appear to influence the spreading of polypropylene on cellulose, the increased hydrophobicity of the cellulose surface[15,16] appears to destroy important hydrogen bonding in the sheets, leading to a decrease in properties. In addition, water-soaked samples showed no additional moisture resistance because of AKD or ASA treatment, even though the cellulose fiber surfaces had become more hydrophobic.

References

1. P. C. Kolosick, C. T. Scott, J. A. Koutsky and G. E. Myers, in *Materials Interactions Relevant to Pulp, Paper, and Wood Industries*, Proc. of Symposium U (Mater. Res. Soc. Nat. Mtg., San Francisco, CA, Apr. 16–20, 1990).
2. D. Maldas and B. V. Kokta, *J. Appl. Polym. Sci.*, **41**, 185 (1990).
3. D. Maldas, B. V. Kokta, R. G. Raj and C. Daneault, *Polymer*, **29**, 1255 (1988).
4. G. E. Myers, P. C. Kolosick, I. S. Chahyadi, et al., in *Materials Interactions Relevant to Pulp, Paper, and Wood Industries*, Proc. of Symposium U (Mater. Res. Soc. Nat. Mtg., San Francisco, CA, Apr. 16–20, 1990).
5. S. Takase and N. Shiraishi, *J. Appl. Polym. Sci.*, **37**, 645 (1989).
6. B. V. Kokta, R. Chen, C. Daneault and J. L. Valade, *Polym. Comps.*, **4**, 229 (1983).
7. R. G. Raj, B. V. Kokta, F. Dembek and B. Sanschagrin, *J. Appl. Polym. Sci.*, **38**, 1987 (1989).
8. S. T. Sean, B. Sanschagrin, B. V. Kokta and D. Maldas, *Mokuzai Gakkaishi*, **36**, 637 (1990).
9. J. M. Felix and P. Gatenholm, *J. Appl. Polym. Sci.*, **42**, 609 (1991).
10. C. E. Farley and R. B. Wasser, in *Sizing of Paper*, ed. by W. F. Reynolds, Tappi Press (1989).
11. B. Evans, in *Sizing of Paper*, ed. by W. F. Reynolds, Tappi Press (1989).
12. D. E. Gunderson, *et al.*, "Reclaiming Fiber from Newsprint-Dry Methods," Submitted to International Conference on Pollution Prevention: Clean Technologies and Clean Products, Proceedings (1990).
13. Technical Association of the Pulp and Paper Industry, *TAPPI Test Methods*, *vol. 1*, 1991.
14. T. Lindstrom and H. O'Brien, *Nord. Pulp and Paper Res. J.*, **1**, 34 (1986).
15. T. Lindstrom and G. Soderberg, *Nord. Pulp and Paper Res. J.*, **1**, 26 (1986).
16. W. C. McCarthy and R. A. Stratton, *Tappi J.*, **70** (12), 117 (1987).
17. V. C. Setterholm, in *Handbook of Physical and Mechanical Testing of Paper and Paperboard*: *vol. 2*, ed. by R. E. Mark. Marcel Dekker, 1984.
18. J. H. Adams, *J. Polym. Sci. pt. A-1*, **8**, 1077–1090 (1970).
19. G. Scott, *Atmospheric Oxidation and Antioxidants*, Elsevier Publishing Co., 1965.
20. J. M. Felix and P. Gatenholm, *Polymeric Materials Science and Engineering*, Proceedings of the American Chemical Society, vol. 64, American Chemical Society, 1991.