COMPOSITE PAPERS

# Strength properties of wood–PE composites: Influence of pulp ratio and pretreatment of PE fibers

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## ABSTRACT

*Composite sheets were formed by blending synthetic polyethylene (PE) pulp and conventional wood pulps. Sheets were pressed at 5500 psi for 5 min at 110°C. Pulp ratios ranged from pure PE to pure wood pulp, with sheet strength increasing with wood-pulp content. However, sheet strength also was improved by pretreating PE fibers with ozone or oxygen–fluorine gas. Improvement was remarkable in the case of oxygen–fluorine pretreatment. The extent of polymer treatment was evaluated using $I_{sp}$, a measure of the specific (acid–base) interactions at the fiber surface. $I_{sp}$ was calculated from a classical equation using data from inverse gas chromatography. The increase in $I_{sp}$ showed linear correlations with the increased strength properties of the composite sheets.*

***Application:***

*The strength of composite papers containing polyethylene (PE) and kraft fibers can be increased by pretreating the PE fibers with oxygen–fluorine gas. Sheet strength approaches that of pure kraft.*


NATURAL ORGANIC REINFORCEments, such as wood fiber, are slowly penetrating the fiber-reinforced thermoplastics market. The relatively low degradation temperature of wood fibers (200°C) dictates the use of thermoplastics with low melting temperatures. To date, polyolefins have been successfully combined with wood fiber. Such composite materials are generally molded by compression *(1, 2)* or by injection *(2)*, where fiber dispersion and fiber–matrix adhesion are the two main factors that have been extensively studied.

Paper is by far the oldest and most economically significant wood-fiber composite. Paper sheets are formed by filtering the pulp, which is dispersed in water, followed by pressing and drying. If the fibers were oriented randomly throughout the sheet, material behavior would be isotropic. However, the hydrodynamic forces on the paper machine orient the fibers in the machine direction, producing an orthotropic material.

Pulps from synthetic polymers have been patented for more than 15 years *(3–5)*. Synthetic pulp has found many applications, including wallpaper, tea bags, wet-lay nonwovens, filters, and textured compounds. In some paper and board applications, the uncommon properties conferred by synthetic pulps—very high opacity and brightness, unusual porosity effects, embossability, dimensional stability—justify their use.

Composites of polymer matrix reinforced with wood fiber are prepared by blending polyolefin synthetic pulps in various proportions with wood fiber. In paper and board manufacture, polyolefin pulps can be fused by raising the temperature of the sheet above 130°C for polyethylene and 165°C for polypropylene, or by using a combination of pressure and lower temperatures close to their melting points. Back and Carlson *(6)* reported detailed studies for certain compositions. Fusion had a dramatic effect on the physical properties of paper and board containing polyolefin synthetic pulps, and the magnitude of the effect depended on the synthetic pulp content. Opacity decreased dramatically after fusion, while the strength properties of papers and boards containing synthetic pulp were considerably improved through thermal consolidation *(7)*.

In terms of paper-machine operability, there are no significant problems caused by the use of polyolefin pulps *(7)*. However, some special attention and modifications are required because of the obvious difference between polyolefin and wood fibers. For instance, working temperatures must not go beyond the melting point.

Considerable work relating wood fiber properties to respective paper properties has been carried out over the years *(8–10)*. The results show that the strength and morphology of fibers have a strong influence on the papermaking process and on product quality. The two factors that largely influence the strength of a sheet of paper *(11–13)* are:

1. The strength of the individual fibers
2. Bonding strength throughout the matrix, which depends on the strength of the individual bonds and the number of bonds.

Seth *(14)* demonstrated how three intrinsic fiber properties—length, strength, and coarseness—affect the papermaking process and product quality. He showed that if we ignore the negative effect of fiber length on sheet formation, longer fibers improve all tensile properties, tearing resistance, and folding endurance, particularly for weakly bonded sheets. However, he

noted that fiber length is less important if the sheets are well bonded through strong interfiber adhesion, since sheet failure is then controlled by the strength of the fibers *(14)*.

The effect of polymer strength additives on bond strength between cellulosic fibers was studied by Russell *et al. (15)*, who examined the use of polyaminoamide epichlorohydrin (PAE) resin (1–2% pulp content). Years later, Espy *(16)* showed that sheet strength properties could be increased by adding PAE (1% pulp content), which is a cationic polymer, and then adding carboxymethyl cellulose (0.4% pulp content), which is an anionic polymer, to dilute suspensions of cellulosic fiber. Stratton and Colson *(17)* recently demonstrated that polymeric strength additives promote fiber–fiber interactions through covalent or ionic bonds, increasing fiber–fiber bond strength by a factor of two or more.

## OBJECTIVE

We mention the emergence of wood-reinforced thermoplastics and cite research into polymeric strength additives as a prelude to the topic of this paper: the use of PE pulp fibers in composite papers containing wood pulp. We focus here on the effect of chemical treatments of PE pulp fibers on the strength properties of PE sheets or sheets containing blends of PE and wood (kraft or explosion) pulps. Specifically, we examine the use of ozone *(18, 19)* and oxygen–fluorine gas *(20)* treatments as methods of enhancing sheet strength through surface modification of PE fibers.

In previous research, we used XPS spectroscopy (photoelectron spectroscopy, also known as ESCA) to show that oxyfluorination produced a large increase in the surface concentration of fluorine and oxygen as hydroxyl and carbonyl groups *(20)*. In subsequent research, we applied inverse gas chromatography (IGC) to these fiber materials *(21)*. IGC gives results analogous to those of contact angle (wetting measurements) while eliminating some of the problems with measurements involving single fibers.

In this paper, we present the specific interaction parameter, $I_{sp}$, as calculated from previous IGC results *(21)*. The $I_{sp}$ parameter—a measure of the specific (acid–base) interactions at the fiber surface—is shown to be sensitive to PE fiber treatments, with an increase in $I_{sp}$ translating to an increase in sheet strength.

## EXPERIMENTAL PROCEDURES

### *Pulp*

A commercial PE pulp fiber was used in this study (PulPlus QP 3850, DuPont). According to the manufacturer, a wetting agent—polyvinyl alcohol and polyvinyl acetate—is introduced into the polymer solution before flash spinning. A full description of this pulp is available in the literature *(18, 19)*.

Two hardwood pulps were used in this study: an explosion pulp made from aspen *(22)* and a kraft pulp made from birch. Our objective here is not to characterize these pulps in terms of cooking conditions, drainage index, refining energy, kappa number, etc. Rather, our interest lies in the study of

1. The effect of blending wood pulp with PE pulp fiber on paper properties (especially breaking length, burst index, and tear index)
2. The effect of ozone and oxygen–fluorine gas treatments carried out on PE pulp fiber.

### *Pretreatment of PE pulp*

Ozone gas was generated from oxygen in a laboratory ozonator (Model 8340, Mathieson). The ozone gas was passed through a dilute aqueous slurry of PE pulp (about 1.2% $O_3$ uptake based on fiber weight) *(19)*. A thorough experimental description of this ozonation procedure is available in the literature *(18, 19)*. PE pulp fiber was also chemically modified via a reactive gas treatment ($F_2$ and $O_2$). Two fluorination levels were carried out by a cooperating vendor (Air Products and Chemicals, Inc.) *(20)*.

### *Papermaking*

PE pulps (treated and untreated) were blended either with kraft or explosion pulp at different proportions, from zero to 100%, based on weight. The sheets produced from the various pulp combinations are described in **Table I**. The sheet numbers from Table I are used in the discussion of results throughout the rest of this report.

Pulps were disintegrated and homogenized in a water suspension. A conventional sheet former was used to produce laboratory handsheets (with an area of 200 $cm^2$ and anhydrous weight of 1.2 g) prepared according to CPPA standard methods. The handsheets were then pressed for 5 min at 5500 psi and 110°C. (Melting temperature of the PE pulp fiber was approximately 140°C.) The effects of temperature, pressure, and pressing time on sheet properties were not studied in this work. At least seven sheets of paper were made for each combination. The samples were then stored in a controlled-humidity room at 50% RH for several days.

The strength properties that we measured were breaking length (km), burst index ($kPa \cdot m^2/g$), and tear index ($mN \cdot m^2/g$). The error bars appearing in the figures are standard deviations calculated on at least ten samples. Sheet grammage ($g/m^2$), thickness (mm), water content (%), and optical properties were also measured and will be presented in a separate report *(23)*.

## RESULTS AND DISCUSSION

In previous works, we showed that both ozone and oxygen–fluorine gas treatments changed the surface chemical composition of PE pulp fibers *(18, 20)* and increased its acid–base characteristics *(21)*. We also found that the surfaces of the kraft and explosion pulp fibers displayed amphoteric and strong basic

characteristics, respectively *(21)*. In the present study, we examine sheet strength properties with regard to PE pulp proportion and interfiber acid–base interactions.

### *Strength properties*

***Breaking length.*** **Figure 1** shows the effect of ozone treatment on breaking length for sheets produced from blends of PE pulp and wood pulp. The breaking length of 100% PE sheets was much lower than that of sheets containing either 100% kraft or explosion pulp. Ozonation further decreased the breaking length of sheets containing 100% PE, although this was not the case for sheets containing blends of PE and wood pulp.

The decrease in breaking length for 100% PE sheets may be due to the pulp's high water content after ozone treatment. The water content of 100% PE sheets (in equilibrium with air at 50% RH) was about 7.5% for sheets produced from pulps that were ozonized for 1.5–2.5 h. In contrast, water content was only 0.5% for sheets prepared from PE pulps that were not treated with ozone *(23)*.

The breaking length of composite sheets increased with increasing proportions of wood pulp. Breaking length was slightly improved by the ozone treatment of PE pulp fiber. Ozonation time of 1.5–2.5 hours seems to reach its optimum level without fiber degradation, as shown in previous work *(18, 21)*.

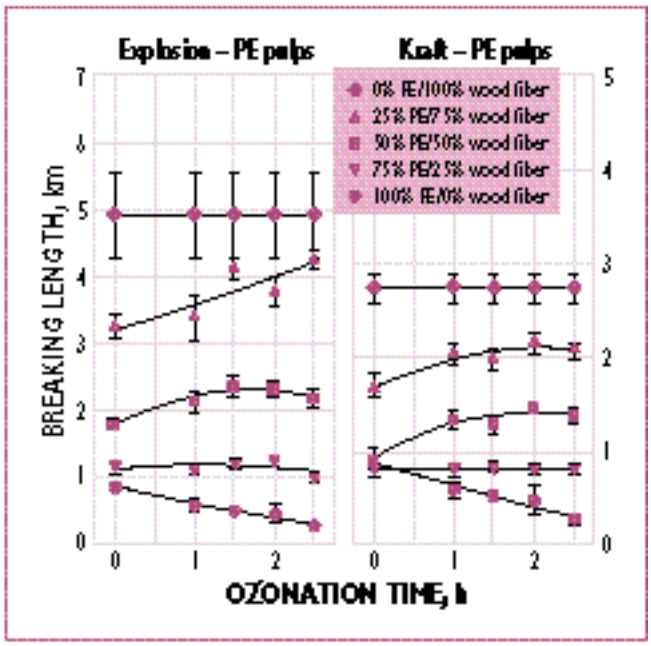
**Figure 2** shows the effect of oxyfluorination treatment on breaking length for sheets produced from PE–wood blends. Again, breaking length increased with increasing wood-pulp content. However, Fig. 2 also shows that breaking length for PE and PE–wood blends increased with the oxyfluorination treatment. Indeed, at the highest level of oxyfluorination (level 2), sheets containing 75% wood pulp and 25% PE pulp had the same breaking length as sheets containing 100% wood pulp. However, even at the higher level of oxyfluorination (level 2), sheets containing 100% PE had a breaking length of only 1.9 km, much lower than the breaking length of 100% kraft sheets (2.7 km) or 100% explosion pulp (5.0 km). This suggests that kraft and explosion pulp fibers are stronger than PE fiber.

Oxyfluorination, especially at level 2, significantly increased the strength and number of bonds between the fibers. This is illustrated by the fact that even though PE pulp

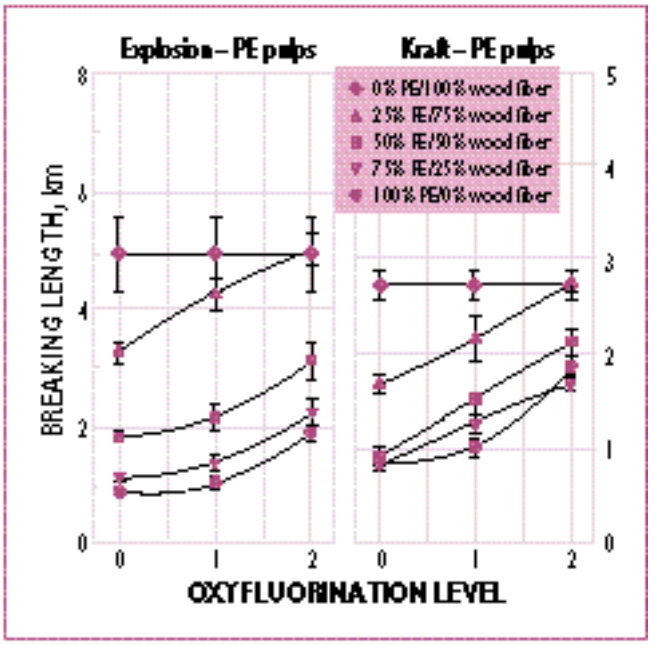
| Sheet no.[b] | PE FIBER TREATMENTS: Ozonation time, h | PE FIBER TREATMENTS: Oxyfluorination level | SHEET FIBER CONTENT, wt.%: PE | SHEET FIBER CONTENT, wt.%: Wood[a] |
|---|---|---|---|---|
| **PURE (100%) PE FIBER** | | | | |
| Untreated PE fibers | | | | |
| 1 | … | … | 100 | … |
| Ozone-treated PE fibers | | | | |
| 2 | 1.0 | … | 100 | … |
| 3 | 1.5 | … | 100 | … |
| 4 | 2.0 | … | 100 | … |
| 5 | 2.5 | … | 100 | … |
| Oxyfluorinated PE fibers | | | | |
| 6 | … | 1 | 100 | … |
| 7 | … | 2 | 100 | … |
| **PURE (100%) WOOD FIBER** | | | | |
| **Kraft** **Explosion[c]** | | | | |
| 8 9 | … | … | … | 100 |
| **BLENDED PE–WOOD FIBERS** | | | | |
| **Kraft** **Explosion[c]** | | | | |
| Untreated PE fibers | | | | |
| 10 31 | … | … | 75 | 25 |
| 11 32 | … | … | 50 | 50 |
| 12 33 | … | … | 25 | 75 |
| Ozone-treated PE fibers | | | | |
| 13 34 | 1.0 | … | 75 | 25 |
| 14 35 | 1.0 | … | 50 | 50 |
| 15 36 | 1.0 | … | 25 | 75 |
| 16 37 | 1.5 | … | 75 | 25 |
| 17 38 | 1.5 | … | 50 | 50 |
| 18 39 | 1.5 | … | 25 | 75 |
| 19 40 | 2.0 | … | 75 | 25 |
| 20 41 | 2.0 | … | 50 | 50 |
| 21 42 | 2.0 | … | 25 | 75 |
| 22 43 | 2.5 | … | 75 | 25 |
| 23 44 | 2.5 | … | 50 | 50 |
| 24 45 | 2.5 | … | 25 | 75 |
| Oxyfluorinated PE fibers | | | | |
| 25 46 | … | 1 | 75 | 25 |
| 26 47 | … | 1 | 50 | 50 |
| 27 48 | … | 1 | 25 | 75 |
| 28 49 | … | 2 | 75 | 25 |
| 29 50 | … | 2 | 50 | 50 |
| 30 51 | … | 2 | 25 | 75 |

[a]Either kraft or explosion-pulp fibers.
[b]The values ascribed to each "Sheet No." throughout this report are based on at least 10 replicate sheets produced at the conditions stated here.
[c]Note that the table is arranged so that the kraft–PE and explosion–PE sheets produced at the same conditions share the same row.

***I. Description of test sheets prepared from blends of PE and wood fibers[a]***




*1. Breaking length as a function of ozone treatment time for PE fibers in sheets containing various blends of PE and wood fibers. Note different scales for kraft and explosion pulps.*




*2. Breaking length as a function of oxyfluorination treatment intensity for PE fibers in sheets containing various blends of PE and wood fibers. Note different scales for kraft and explosion pulps.*

fibers are weaker than wood fibers, the sheets containing a 25%/75% blend of oxyfluorinated PE and wood pulp are as strong as sheets containing 100% wood pulp.

***Burst index.*** **Figure 3** shows the effect of ozone treatment on burst index for sheets produced from blends of PE pulp and wood pulp. Burst index for the sheets containing 100% PE was much lower than for sheets containing 100% wood pulp. As with breaking length, ozonation reduced burst index for sheets containing 100% PE and had a mixed effect on sheets containing PE–wood-pulp blends. The decrease in burst index for the 100% PE sheets may also be due to the water content, which was quite high after ozonation *(23)*. Figure 3 shows that sheets containing 75% kraft and 25% PE had a burst index close to that of sheets made from 100% kraft, especially for PE fibers that were ozonized for 1.5–2.5 h.

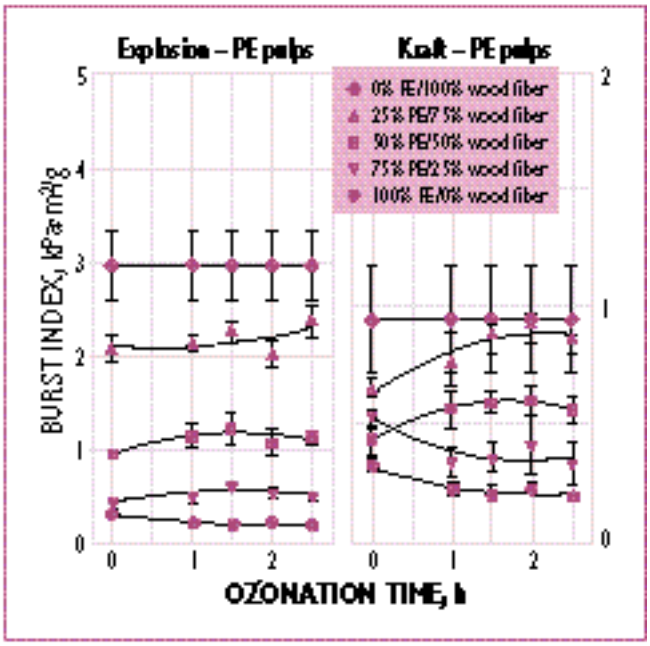
**Figure 4** shows the effect of oxyfluorination treatment on burst index for sheets produced from PE–wood blends. Without oxyfluorination, the burst index of 100% kraft sheets was higher than that of any of the sheets containing PE pulp. However, oxyfluorination had a very positive effect on the burst of PE pulp sheets, and at the highest level of treatment (level 2), all of the sheets containing PE had a higher burst than the sheets of 100% kraft. Burst index for the kraft–PE blends increased with increasing content of oxyfluorinated PE pulp. The highest burst index for the kraft sheets were those containing 25% PE pulp oxyfluorinated at level 2.

Figure 4 also shows similar trends for explosion pulp, with burst index increasing with wood-pulp content and the oxyfluorination level of PE pulp fiber. Sheets containing 75% explosion pulp and 25% oxyfluorinated PE pulp (level 2) had the same burst index as sheets from 100% explosion pulp.

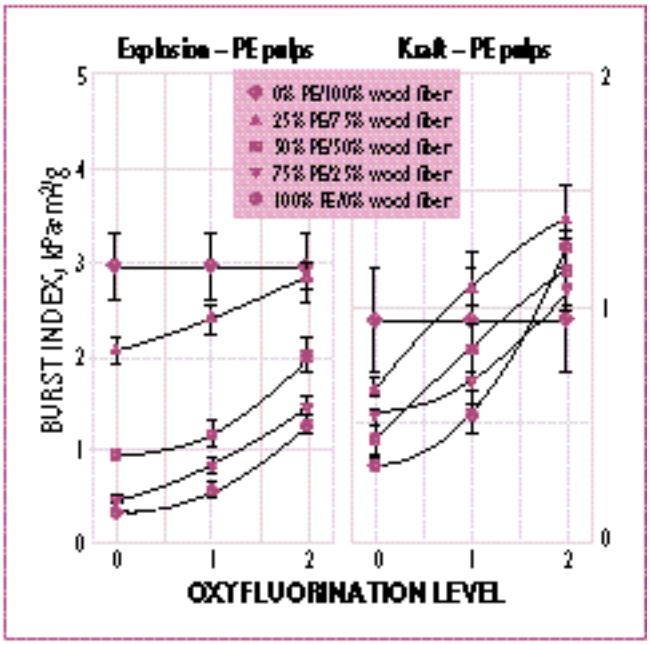
***Tear index.*** **Figure 5** shows that the tear index of sheets containing 100% PE was lower than that of sheets containing 100% kraft or explosion pulp. Ozonation had a negative effect on tear index for the 100% PE sheets, but the effect of ozonation was mixed for the sheets containing blends of PE and wood pulps. Again, the decrease in tear index with increasing ozonation for the sheets containing 100% PE fibers could be explained by the significant increase in the water content of the PE sheets *(23)*.

Sheets containing 75% explosion pulp and 25% ozonized PE pulp (2.5 hours) had a higher tear index than sheets containing 100% explosion pulp. Without ozonation of the PE pulp fiber, sheets containing 25%/75% or 50%/50% mixtures of wood pulp and PE pulp had lower tear indexes than the sheets with 100% PE pulp.

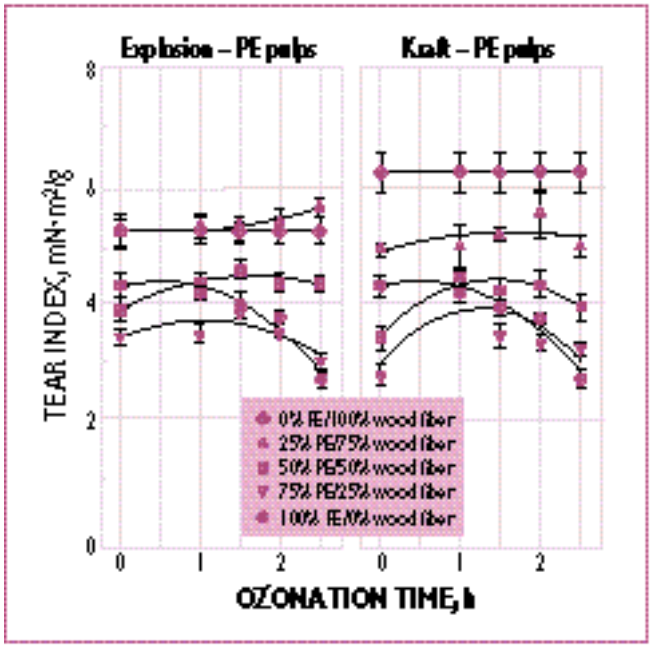
**Figure 6** shows that sheets prepared from blends of kraft pulp and oxyfluorinated PE pulp (level 2) had tear indexes close to that of 100% kraft pulp sheets. The blends of explosion pulp and oxyfluorinated PE pulp had tear indexes higher than sheets from 100% explosion pulp.



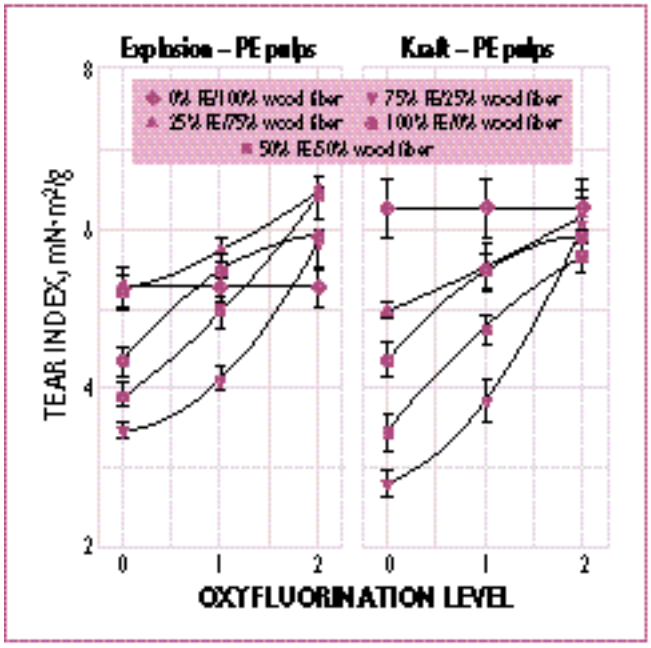

*3. Burst index as a function of ozone treatment time for PE fibers in sheets containing various blends of PE and wood fibers. Note different scales for kraft and explosion pulps.*




*4. Burst index as a function of oxyfluorination treatment intensity for PE fibers in sheets containing various blends of PE and wood fibers. Note different scales for kraft and explosion pulps.*




*5. Tear index as a function of ozone treatment time for PE fibers in sheets containing various blends of PE and wood fibers*




*6. Tear index as a function of oxyfluorination treatment intensity for PE fibers in sheets containing various blends of PE and wood fibers*

Oxyfluorination significantly increased the tear index of the 100% PE pulp paper. At level 2, the 100% PE paper had a higher tear index than the 100% explosion pulp paper.

It is also interesting to note that the tear indexes of sheets containing 25%/75% and 50%/50% blends of wood pulp and PE pulp were lower than the untreated or level-1 oxyfluorinated sheets of 100% PE pulp. These results are hard to explain, suggesting the need for more tests and analyses dealing with all parameters influencing the tear index of paper.

### *Strength properties vs. $I_{sp}$*

Inverse gas chromatography (IGC) has been widely used to characterize

molecular changes in surface composition following chemical treatments *(24, 25)*. The technique involves measuring the enthalpy of adsorption of small polar or nonpolar gas molecules at the substrate surface. Relative acid or basic constants of the fiber surface are obtained by comparing the enthalpy of adsorption of nonpolar and polar molecular "probes." For instance, it is clear that highly acidic surfaces will adhere to highly basic surfaces through acid–base bonds, such as hydrogen bonds, whereas two acidic surfaces or fibers will adhere minimally. Indeed, Schultz and Lavielle *(26)* found a direct relation between acid–base interactions and interfacial shear strength in carbon-fiber–epoxy composites.

In previous work *(21)*, we used IGC analysis to show that ozonized PE pulp fiber surfaces had relative acid constants, $K_a$, of 3.5 and 3.3 (arbitrary units) after 2-h and 3-h ozone treatments, respectively. The relative basic constants, $K_b$, were 0.8 and 1.0, respectively. In contrast, untreated PE pulp fibers have a surface with neutral characteristics, i.e., $K_a \approx K_b \approx 0$. For PE fibers ozonized for 1.5–2.5 h, we attribute the acid constant, $K_a$, as 3.4 and the base constant, $K_b$, as 0.9. In the same work *(21)*, we showed that the surfaces of oxyfluorinated PE fibers (levels 1 and 2) had $K_a$ = 7.3 and 10.3, and $K_b$ = 2.5 and 9.2, respectively. Explosion and kraft pulp fiber had surfaces with $K_a$ = 2.4 and 5.5, and $K_b$ = 12.1 and 5.0, respectively *(21)*. In the following discussion, these acid–base constants are used to estimate the magnitude of specific interactions ($I_{sp}$) between fibers and to examine the contribution of $I_{sp}$ to sheet strength properties.

When a polymeric matrix is reinforced with fiber, the magnitude of $I_{sp}$ between fiber and matrix is estimated according to the following equation *(27)*:

$$I_{sp} = (K_{a,f} K_{b,m}) + (K_{b,f} K_{a,m}) \qquad (1)$$

where

$K_{a,f}$ = relative acid constant for fiber

$K_{a,m}$ = relative acid constant for matrix

$K_{b,f}$ = relative basic constant for fiber

$K_{b,m}$ = relative basic constant for matrix.

To estimate the degree or the level of the specific interactions between two fibers, $I_{sp}$ can be calculated using the following equation:

$$I_{sp} = (K_{a,PE} K_{b,w}) + (K_{b,PE} K_{a,w}) \quad (2)$$

where

$K_{a,PE}$ = relative acid constant for PE fiber

$K_{a,w}$ = relative acid constant for wood fiber

$K_{b,PE}$ = relative basic constant for PE fiber

$K_{b,w}$ = relative basic constant for wood fiber.

Because the fiber–fiber interface in composite papers can be PE–PE, PE–wood, or wood–wood, Eq. 2 is modified to account for this as follows. Let $N_t$ represent the total number of fibers in a composite paper, and let $N_{PE}$ and $N_w$ represent the number of PE and wood fibers in the composite paper (i.e., $N_{PE} + N_w = N_t$). Also, assume that the ratios $N_{PE}/N_t$ and $N_w/N_t$ represent, respectively, the proportions of PE and wood fibers in the composite sheets. To simplify, we can state that the ratios $N_{PE}/N_t$ and $N_w/N_t$ represent the PE and wood weight proportions, $P_{PE}$ and $P_w$, respectively.

Let us now introduce the following probabilities: $\text{Prob}_{i,j}$ is the probability that a fiber $i$ and a fiber $j$ were close to each other in the paper. $C_m^n$ represents the number of combinations, $n$, among $m$ fibers: $C_m^n = m!/[n!(m-n)!]$.

$$\text{Prob}_{PE,PE} = C_{N\,PE}^{\,2}/C_N^{\,2} =$$

$$[N_{PE}(N_{PE}-1)]/[N(N-1)] \approx$$

$$(N_{PE}/N)^2 \approx P_{PE}^{\,2}$$

$$\text{Prob}_{w,w} = C_{N\,w}^{\,2}/C_N^{\,2} =$$

$$[N_w(N_w-1)]/[N(N-1)] \approx (N_w/N)^2 \approx$$

$$P_w^{\,2}$$

$$\text{Prob}_{PE,w} = (C_{NPE}\, C_{Nw})/C_N^{\,2} =$$

$$2(N_{PE}\, N_w)/[N(N-1)] \approx 2P_{PE}\, P_w$$

By introducing these probabilities, Eq. 2 can be transformed to Eq. 3.

$$I_{sp} = [2(P_{PE})^2(K_{a,PE}K_{b,PE})] +$$

$$\{2P_{PE}P_w[(K_{a,PE}K_{b,w})$$

$$+ (K_{b,PE}K_{a,w})]\} +$$

$$[2(P_w)^2(K_{a,w}K_{b,w})] \qquad (3)$$

where the first term represents the contribution of contacts between PE fibers, the second term represents the contribution of PE–wood contacts, and the last term represents the contribution of contacts between wood fibers.

It is important to note that Eq. 3 supposes a perfect and homogeneous dispersion of fibers within the sheet. Also, the effect of fiber orientation is not considered, since this factor should not change with either the paper composition, the treatment of the PE pulp fiber surface, or the papermaking process.

Equation 3 was used to calculate $I_{sp}$ values for the 51 pulp–PE-treatment combinations evaluated in this study. The $I_{sp}$ values in **Table II** clearly demonstrate that the ozone

treatment of the PE pulp fibers had a much smaller effect on the $I_{sp}$ of the 100% PE sheets than fluorination. Ozone treatment provided a maximum $I_{sp}$ of 6.1 (Sheets 3–5), while the two levels of fluorination produced $I_{sp}$ of 36.5 and 189.5 (Sheets 6 and 7). The $I_{sp}$ values for the 100% kraft (Sheet 8) and 100% explosion (Sheet 9) papers were 55.0 and 58.1, respectively.

The high $I_{sp}$ value for Sheet 7 indicates that the strength and number of bonds within this sheet exceeds that of Sheets 8 and 9. However, breaking length for Sheet 7 (100% PE, oxyfluorination level 2) was less than that for Sheets 8 and 9 (100% kraft and 100% explosion pulp, respectively), as seen in Fig. 2. Since sheet strength is largely determined by fiber strength and bond strength *(11–14)*, we can conclude that the strength of an individual PE fiber was much less than that of an individual kraft or explosion fiber. This suggests that if PE pulp could be produced with individual fiber strength similar to that of individual kraft or explosion fiber, oxyfluorination at level 2 would lead to extra-strength PE pulp paper.

***Variation of strength with sheet composition and*** $\mathbf{I}_{sp}$**.** In the following discussion, we examine the $I_{sp}$ values for the 51 test sheets (Table II) in an effort to find correlations between this parameter and sheet strength properties.

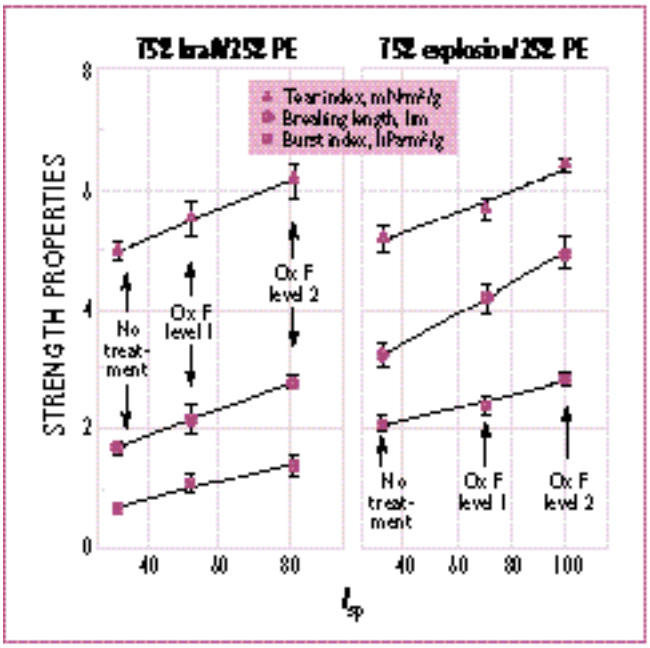
The $I_{sp}$ values for all of the groups in Table II increase with increasing wood-fiber content, with one exception. Group 7—representing sheets containing PE fibers oxyfluorinated to level 2—reverses the trend, with $I_{sp}$ decreasing with wood-fiber content. We have already noted that sheet strength depends on individual fiber strength and on the number and strength of individual bonds. However, in the case of composite sheets containing PE fibers, we have two conflicting trends:

1. Fiber strength decreases with increasing PE fiber content.

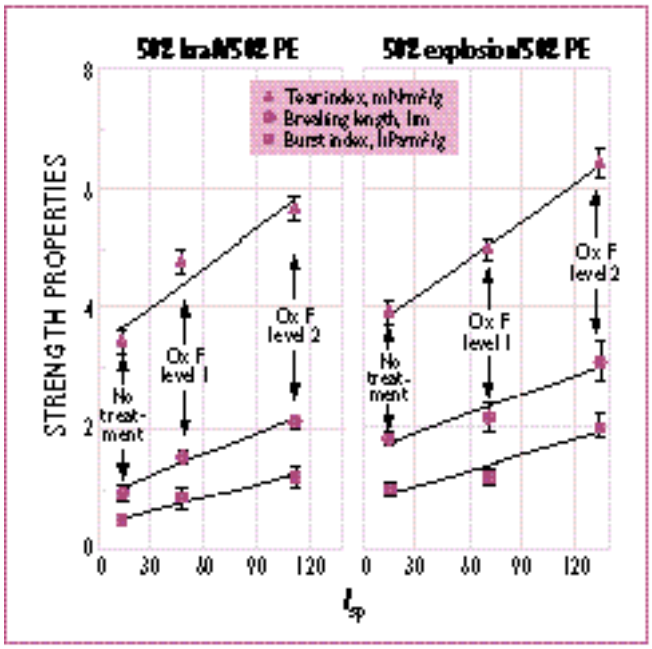
| PE–wood-fiber ratio, wt.% | UNTREATED PE FIBERS | | OZONE-TREATED PE FIBERS | | | | | | OXYFLUORINATED PE FIBERS | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 1.0 hour[a] | | 1.5 hour | | 2.0 hour | | 2.5 hour | | Level 1 | | Level 2 | |
| | Sheet no.[b] | $I_{sp}$ | Sheet no.[b] | $I_{sp}$ | Sheet no.[b] | $I_{sp}$ | Sheet no.[b] | $I_{sp}$ | Sheet no.[b] | $I_{sp}$ | Sheet no.[b] | $I_{sp}$ | Sheet no.[b] | $I_{sp}$ |
| | Group 1 | | Group 2 | | Group 3 | | Group 4 | | Group 5 | | Group 6 | | Group 7 | |
| **Kraft pulp fibers** | | | | | | | | | | | | | | |
| 100 PE | 1 | 0 | 2 | 1.5 | 3 | 6.1 | 4 | 6.1 | 5 | 6.1 | 6 | 36.5 | 7 | 189.5 |
| 75/25 PE–kraft | 10 | 3.4 | 13 | 8.4 | 16 | 15.1 | 19 | 15.1 | 22 | 15.1 | 25 | 42.8 | 28 | 148.3 |
| 50/50 PE–kraft | 11 | 13.8 | 14 | 19.6 | 17 | 26.3 | 20 | 26.3 | 23 | 26.3 | 26 | 48.0 | 29 | 112.2 |
| 25/75 PE–kraft | 12 | 30.9 | 15 | 35.1 | 18 | 39.6 | 21 | 39.6 | 24 | 39.6 | 27 | 52.1 | 30 | 81.1 |
| 100 kraft | 8 | 55.0 | 8 | 55.0 | 8 | 55.0 | 8 | 55.0 | 8 | 55.0 | 8 | 55.0 | 8 | 55.0 |
| **Explosion pulp fibers** | | | | | | | | | | | | | | |
| 100 PE | 1 | 0 | 2 | 1.5 | 3 | 6.1 | 4 | 6.1 | 5 | 6.1 | 6 | 36.5 | 7 | 189.5 |
| 75/25 PE–explosion | 31 | 3.6 | 34 | 12.6 | 37 | 23.3 | 40 | 23.3 | 43 | 23.3 | 46 | 59.5 | 49 | 165.3 |
| 50/50 PE–explosion | 32 | 14.5 | 35 | 25.7 | 38 | 37.7 | 41 | 37.7 | 44 | 37.7 | 47 | 70.8 | 50 | 135.3 |
| 25/75 PE–explosion | 33 | 32.7 | 36 | 40.9 | 39 | 49.3 | 42 | 49.3 | 45 | 49.3 | 48 | 70.3 | 51 | 99.5 |
| 100 explosion | 9 | 58.1 | 9 | 58.1 | 9 | 58.1 | 9 | 58.1 | 9 | 58.1 | 9 | 58.1 | 9 | 58.1 |

[a] $K_a$ and $K_b$ for the 1-h ozonized PE pulp fiber were estimated at 1.7 and 0.45, respectively.
[b] The values ascribed to each "Sheet No." throughout this report are based on at least ten measurements on at least seven replicate sheets.

***II. Specific interaction parameter*** ($\mathbf{I}_{sp}$) ***illustrating the contribution of the acid–base interactions with regard to interfiber adhesion of various paper sheets described in Table I, as calculated using Eq. 3***




*7. Strength properties of wood–PE sheets (75%/25%) as a function of $I_{sp}$ at three levels of oxyfluorination*




*8. Strength properties of wood–PE sheets (50%/50%) as a function of $I_{sp}$ at three levels of oxyfluorination*

2. Fiber bonding increases with increasing proportion of PE fibers oxyfluorinated at level 2.

As seen in Fig. 2, breaking length at fluorination level 2 increased with increasing wood-fiber content for explosion–PE pulps, even though $I_{sp}$ decreased with increasing wood-fiber content. Kraft–PE pulps showed a similar trend. These results suggest that the effect of fiber strength on breaking length is greater than the enhanced bonding provided by the oxyfluorinated PE.

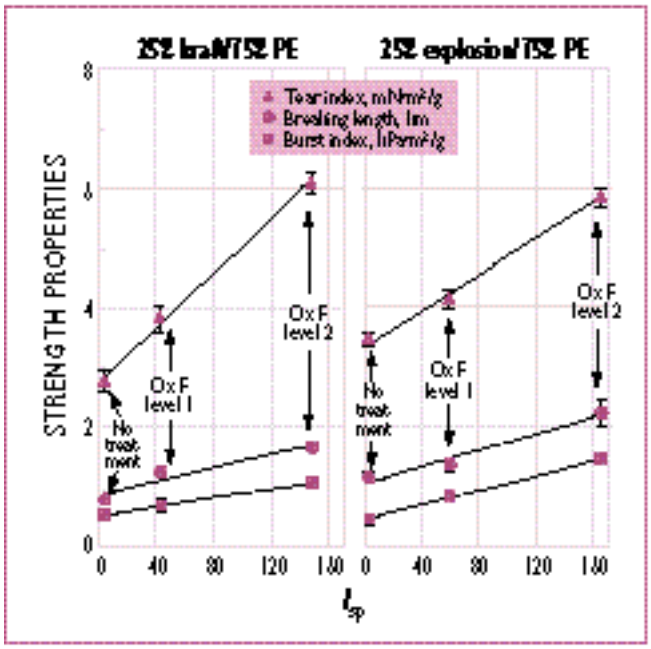
Figure 4 shows the same trend for burst index at fluorination level 2 for explosion–PE sheets, with burst index increasing with increasing wood-fiber content despite the steady decline in $I_{sp}$. However, burst index for the kraft–PE sheets had a more complex response at oxyfluorination level 2. The 100% kraft sheets had the lowest burst index, while the 100% PE sheets had the second highest burst index.

Tear index for the kraft–PE and explosion–PE sheets also had a complex response at oxyfluorination level 2, as seen in Fig. 6, with no clear correlation between $I_{sp}$ and tear index. The lack of correlation is very clear for the sheets containing PE oxyfluorinated at level 1. Sheets with 100% PE, 75% PE, and 50% PE show a steady decline in $I_{sp}$, but the corresponding tear indexes do not show the same pattern. Again, these trends can be explained by the movement of individual fiber strength and bond strength (based on the strength and number of bonds) in opposite directions.

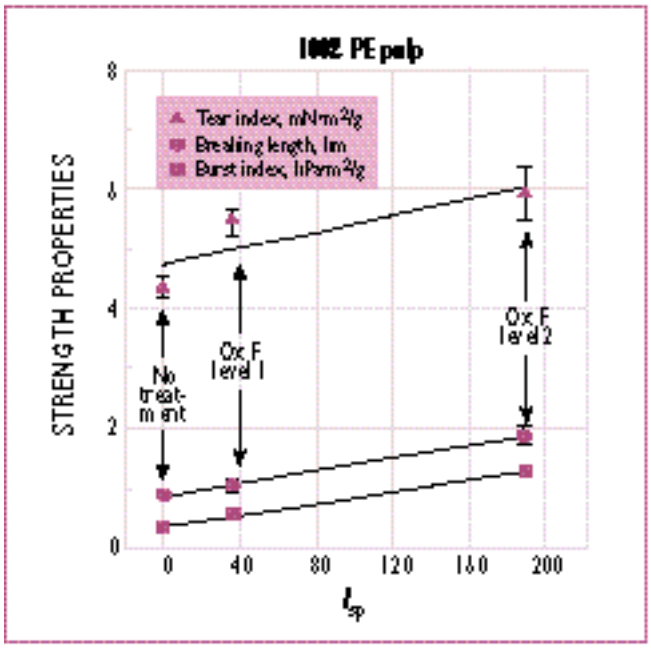
Within a given treatment level, the variation in tear index with the change in pulp proportions (Figs. 5 and 6), does not follow the variation in the $I_{sp}$ value (Table II). However, at constant pulp proportions, the change in tear index with the treatment of the PE pulp does follow the change in the $I_{sp}$ value, especially for the oxyfluorination treatments. At constant pulp proportions, the changes in breaking length (Figs. 1 and 2) and burst index (Figs. 3 and 4) of the paper sheets showed even more agreement with the variation of the $I_{sp}$ values (Table II) than did the changes in tear index (Figs. 5 and 6).

***Correlation of paper strength with $I_{sp}$.*** We can examine the variations of the strength properties as a function of $I_{sp}$ according to the treatment of the PE fiber surface at constant pulp proportions. For instance, consider the $I_{sp}$ of kraft–PE Sheets 12, 27, and 30 (25%PE/75% kraft containing untreated PE and oxyfluorinated PE at levels 1 and 2, respectively) and explosion–PE Sheets 33, 48, and 51 (25%PE/75% explosion pulp containing untreated PE and oxyfluorinated PE at levels 1 and 2, respectively). $I_{sp}$ increases with increasing oxyfluorination: 30.9, 52.1, and 81.1 for the kraft–PE sheets and 32.7, 70.3, and 99.5 for the explosion–PE sheets. **Figure 7** shows linear correlations between the strength properties of these sheets and their respective $I_{sp}$. **Figures 8 and 9** also show linear correlations between strength properties and $I_{sp}$ values for sheets containing 50% and 75% oxyfluorinated PE fibers, respectively. **Figure 10** shows the correlations for sheets containing 100% PE fibers. Breaking length and burst index increase linearly along with the rise in $I_{sp}$ in response to the oxyfluorination treatment, but this was not quite the case for tear index.

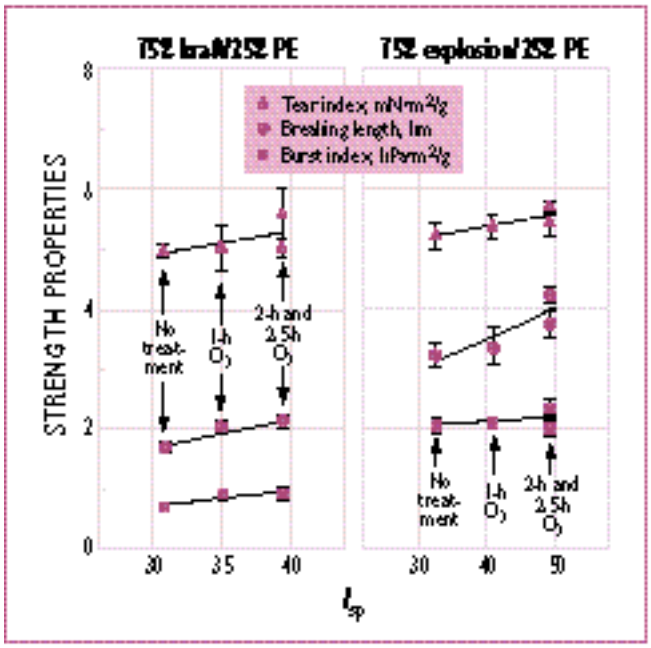
As for the ozone treatment, the results in Table II show that ozonation increased the $I_{sp}$ only slightly. For



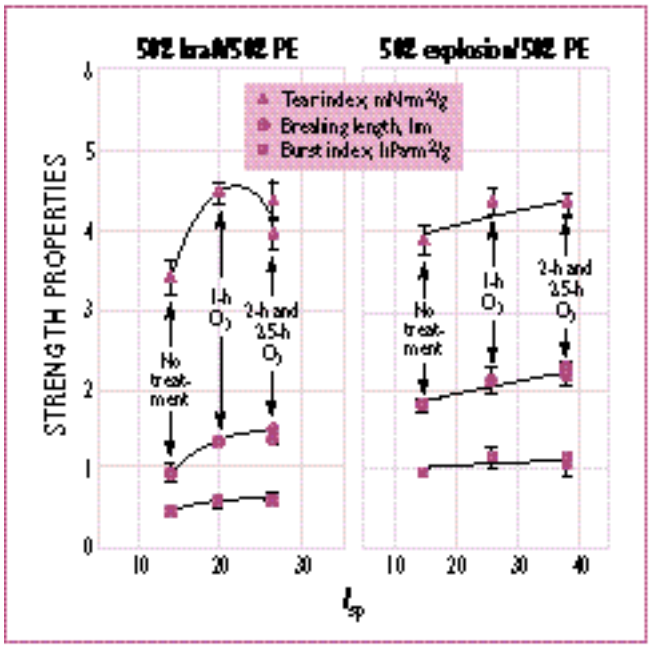

*9. Strength properties of wood–PE sheets (25%/75%) as a function of $I_{sp}$ at three levels of oxyfluorination*




*10. Strength properties of 100% PE sheets as a function of $I_{sp}$ at three levels of oxyfluorination*

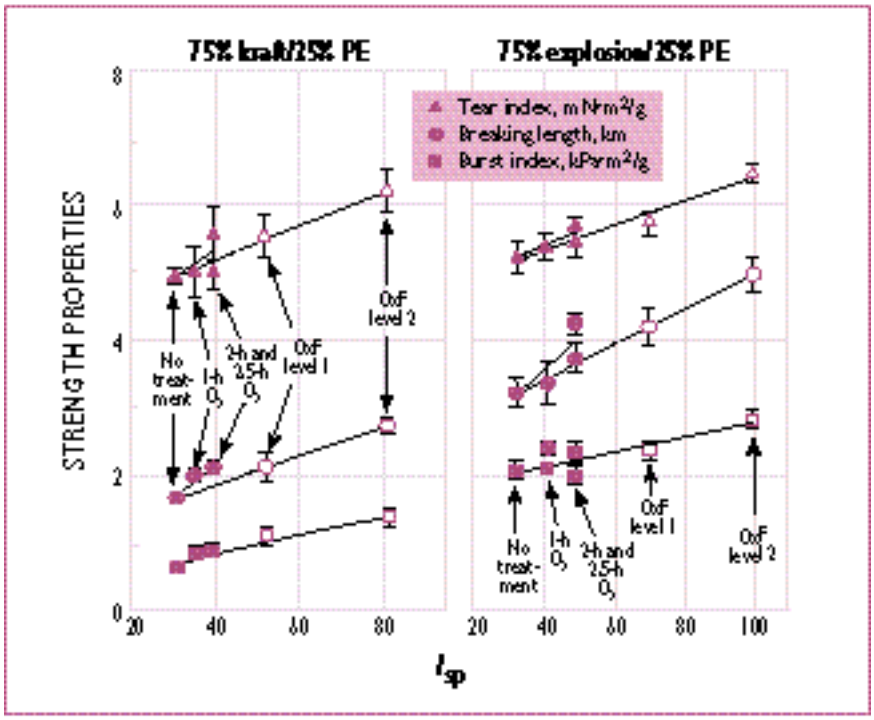



*11. Strength properties of wood–PE sheets (75%/25%) as a function of $I_{sp}$ at four levels of ozonation*




*12. Strength properties of wood–PE sheets (50%/50%) as a function of $I_{sp}$ at four levels of ozonation*

instance, for the sheets containing 75% kraft pulp and 25% ozone-treated PE fibers (Sheets 12, 15, 18, 21, and 24), the corresponding $I_{sp}$ values were 30.9, 35.1, 39.6, 39.6, and 39.6, respectively. **Figures 11 and 12** show the variations of the strength properties as a function of $I_{sp}$ at three levels of ozone treatment (1 h, 2 h, and 2.5 h) for 75%/25% and 50%/50% wood–PE sheets, respectively. Although the $I_{sp}$ value did not increase greatly in response to ozonation of the PE pulp, linear correlations could be observed in small $I_{sp}$ ranges, as shown in Fig. 11. For papers containing 50% explosion pulp blended with 50% PE pulp, Fig. 12 shows a linear correlation between strength properties and $I_{sp}$ with increasing ozonation of PE fibers. This was not the case for sheets containing 50% kraft pulp blended with 50% PE pulp (Fig. 12),




*13. Strength properties of wood–PE sheets (75%/25%) as a function of $I_{sp}$ at various levels of PE-fiber pretreatment*

where the $I_{sp}$ range was relatively small, and linear correlations could not be drawn, especially for tear index.

***Origin of enhanced adhesion for treated PE fibers.*** Introduction of specific (acid–base) interactions is not the only factor influencing paper strength properties. Changes in the structural and morphological properties of the PE fiber surface in response to ozonation and oxyfluorination treatments certainly influence interfiber adhesion and thus the strength properties of composite paper. However, these properties were not characterized in this study. Nevertheless, it was shown that the strength properties of composite paper correlate linearly with the specific interaction parameter, $I_{sp}$, which represents the acid–base interactions.

For comparison, **Fig. 13** illustrates the effects of ozonation and oxyfluorination treatments on $I_{sp}$ and on the strength properties of composite sheets containing 75% wood fiber and 25% PE. Note the $I_{sp}$ range of each treatment. The maximum $I_{sp}$ for blends of ozone-treated PE and wood fiber never exceeded 50 (arbitrary units). Note also that the linear correlations obtained through ozonation and oxyfluorination were approximately the same (roughly the same slopes), especially for burst and tear indexes. The slopes obtained for breaking length in the ozonation $I_{sp}$ range were somewhat higher than those observed for the oxyfluorination treatment.

As previously noted, Eq. 3 breaks down the $I_{sp}$ parameter into three terms describing interactions between PE–PE, PE–wood, and wood–wood fibers. For the 75%/25% PE-kraft sheet (Sheet 28, oxyfluorinated, level 2), these terms are, respectively, 106, 38, and 3. Thus, acid–base interactions between treated PE fibers contribute to a large extent to the enhanced properties. For the opposite case, the 25%/75% PE–kraft sheet (Sheet 30, oxyfluorinated, level 2), the corresponding three terms are 12, 38, and 31. In this case, the middle term, due to unlike interfiber contacts, is dominant, but the overall $I_{sp}$ is lower. This skewed contribution of oxyfluorinated PE fibers to adhesion is due to its highly polar and amphoteric character, as evidenced by its high acidic ($K_a$ = 10.3) and basic ($K_b$ = 9.2) constants. The result is a strong dependence of paper strength on paper composition, especially in the case of Sheet 28.

On a more fundamental point of view, the enhancement of properties obtained through the oxyfluorination treatment originates, in addition to conventional hydrogen bond (C = O···H–O–), in other interfiber hydrogen bonds, such as –C–F···H–O–. These have been demonstrated to involve energies in the range of 9 kJ/mol *(28)*, which is about half of the energy of a conventional hydrogen bond. These bonds have been detected in synthetic polymer blends such as poly(vinylidene fluoride)–poly(methyl methacrylate) blends, which are miscible, because of a similar specific interaction *(29)*. Some investigations have been carried out by other workers *(30)*, especially on PE and polypropylene films, showing enhanced adhesion following oxyfluorination.

## CONCLUSION

Composite papers containing PE pulp fibers were produced using a conventional papermaking process augmented by hot pressing and drying. The addition of wood fibers (kraft or explosion pulps) to the PE pulp fiber improved sheet strength properties.

PE pulp fibers were subjected to ozone treatment or oxyfluorination in an effort to modify the fiber surface and improve interfiber adhesion. The effects of PE fiber treat-

**KEYWORDS**
*Gas chromatography, lignocellulose, polyethylene, mechanical properties, fiber bonding, kraft papers, explosion pulping, equations, oxygen fluorides, ozone, parameters, polymer paper combinations, bibliographies.*

ment on sheet properties were evaluated by developing a value for the specific (acid–base) interaction parameter, $I_{sp}$, at each combination of pulp ratio and fiber treatment. The $I_{sp}$ was calculated using an equation based on the Saint Flour and Papirer $I_{sp}$ equation *(27)*, taking into account the proportion of blended pulp. Inverse gas chromatography (IGC) was used to obtain the data required for calculation of $I_{sp}$.

Both the ozone treatment and oxyfluorination modified the surface of the PE fibers, leading to improved interfiber adhesion and greater sheet strength. Linear correlations were observed between sheet strength properties and the $I_{sp}$ parameter. These improvements were remarkable in the case of oxyfluorination, which significantly increased the specific (acid–base) interactions at the fiber–fiber interface.

The principal focus of this study was to examine the effects of PE pretreatments on specific (acid–base) interactions and thus on interfiber adhesion. Clearly, interfiber adhesion is also related to nonspecific interactions and to mechanical adhesion due to fiber entanglement and hot pressing. Nevertheless, linear correlations between $I_{sp}$ and sheet strength were obtained, even though these latter factors were not considered in this study.

The effect of fiber strength on sheet strength also was not directly considered in this study, since we knew that the strength of individual PE fibers is much lower than that of wood fibers. However, the results suggest that if manufacturers can develop stronger PE pulp fibers with higher aspect ratios, oxyfluorination could provide composite papers with very interesting strength properties.

Finally, the linear correlations between $I_{sp}$ and sheet strength suggest that IGC could be a useful technique for evaluating surface treatment, or even chemical pulping techniques, in order to maximize interfiber adhesion. **TJ**

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*The authors thank DuPont company for its generous gift of synthetic pulp fiber; Air Products for the oxyfluorination treatments; as well as the Natural Sciences and Engineering Research Council of Canada, the Fonds pour la formation de chercheurs et l'aide à la recherche of Quebec, and the Tunisian Government for their financial support.*

*Received for review Jan. 3, 1995.*
*Accepted March 20, 1996.*

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