

## Preparation of a Microporous Composite: Encapsulation of Paper by Polyethylene

B. FISA and R. H. MARCHESSAULT, *Department of Chemistry,  
Université de Montréal, Montreal 101, Quebec, Canada*

### Synopsis

A rapid polymerization method for *in situ* synthesis of polyethylene in a typical paper matrix of cellulose fibers is described. The unique properties of this double matrix, polyethylene in cellulose, are the result of performing the polymerization in a non-solvent such that simultaneous polymerization and crystallization takes place yielding a nascent morphology. The morphology has been studied by scanning electron microscopy and was found to be different from what is usually obtained for melt crystallized polyolefins. Optical microscopy shows the polyethylene to be present as a complementary matrix with respect to the basic fiber construct. Mechanical, optical, and other properties of encapsulated filter paper have been measured using standard TAPPI tests. The results show a general improvement in physical properties for a range of "add ons" from 0 to 27%. Wet-strength and opacity undergo major changes.

### INTRODUCTION

Modification of cellulosic materials by admixing them with preformed synthetic polymers has been practiced for many years. Some of these techniques such as coating of paper have found widespread industrial use. Methods involving polymer synthesis in the presence of cellulosic substrate have also been extensively studied. Broad changes in cellulose properties including hydrophobicity, rot resistance, fabric hand changes, porosity dimensional stability, and dyeing and printing characteristics can be achieved by one of the following techniques: grafting,<sup>1</sup> *in situ* polymerization,<sup>2</sup> interfacial polymerization,<sup>3</sup> or encapsulation. The latter technique, which is the subject of this paper, involves a polymerization catalyst deposited onto or adsorbed by cellulose and subsequent polymerization of a convenient monomer. A product retaining the form and core properties of cellulose fiber but having the surface properties of the polymer is then obtained. One early example of encapsulation<sup>4</sup> involved adsorption of boron trifluoride by the cellulose and low-temperature cationic polymerization of isobutylene or  $\alpha$ -methylstyrene. The paper treated with 8-10% polyisobutylene was impervious to water in liquid form.

Transition metal catalysts (Ziegler-Natta type) can also be, under certain conditions, deposited onto the cellulose. For example, Herman et al.<sup>5,6</sup> described a process that can be summarized as follows: an organometallic,

most often triethylaluminum, is added to a dry cellulose suspension in a  $\text{TiCl}_4$ -hydrocarbon mixture. The products of the reaction between  $\text{TiCl}_4$  and triethylaluminum are insoluble in the hydrocarbon solvent and precipitate onto the cellulose. When the precipitation is nearly complete, a monomer (for example, ethylene) is bubbled through the suspension of the "activated" substrate; and since the resultant polymer is usually insoluble in the polymerization medium, it remains where it was formed, i.e., on the substrate surface. Using this process, individual fibers could be coated with polyethylene, polypropylene, or other polyolefins. An important feature of the process which assures its success is the fundamental affinity of transition metal halides to cellulosic substrate.<sup>7</sup> This process has been used predominantly to encapsulate individual pulp fibers with polyethylene, and these were subsequently formed into sheets using conventional papermaking techniques.<sup>8</sup> The main drawback of the above technique<sup>5</sup> is that the catalyst is formed outside the fiber surface, and it is usually a matter of minutes before precipitation onto the fiber is completed. During this time, small catalyst microcrystals form larger aggregates before they deposit on the substrate, making the catalyst texture rather uneven.<sup>7</sup> Since the polymerization occurs on the solid catalytic surface, distribution of the polymer on the fiber is not very uniform. On the other hand, when a sheet is made from the encapsulated fibers, interfiber hydrogen bonds typical for a paper sheet are replaced by plastic bond, thus giving the product more plastic-like character. When a preformed paper sheet is encapsulated, it is expected that most if not all existing interfiber hydrogen bonds are maintained.

This work deals with encapsulation of model paper substrate with polyethylene, using the same catalytic system [ $\text{TiCl}_4/\text{Al}(\text{C}_2\text{H}_5)_3$ ] as Herman et al.<sup>5</sup> However, while the technique described is suitable for depositing the catalyst on the surface of individual fibers in a slurry, it does not lend itself to providing a uniform deposition throughout a matrix of paper or any other microporous construction. Since the catalyst particles precipitate, generally, on the outer surface of the substrate, only the exterior of the paper is coated. For this reason, it is necessary to generate the catalyst within the paper matrix. Several methods could be used. For example,  $\text{VCl}_4$  decomposes thermally, giving insoluble  $\text{VCl}_3$ .<sup>9</sup> Soaking the paper with a catalyst, e.g.,  $\text{TiCl}_4/\text{Al}(\text{iso-C}_4\text{H}_9)_3$ ,<sup>10</sup> which is soluble in hydrocarbons when prepared at low temperatures ( $-80^\circ\text{C}$ ) but precipitates irreversibly when heated to around  $-30^\circ\text{C}$ , might also give satisfactory results. However, the simplest way to achieve similar results seems to be the treatment of the paper with a solution of  $\text{TiCl}_4$  in a solvent with low boiling point (isopentane, butane, etc.). Dipping the paper in such a mixture and subsequent passage into an evaporation zone results in a preferential removal of hydrocarbon solvent, leaving dispersed  $\text{TiCl}_4$  throughout the paper matrix. The sheet is subsequently brought in contact with organometallic, either in solution or vapor, thus forming the insoluble heterogeneous Ziegler-Natta catalyst in a finely dispersed form.

TABLE I  
Polyethylene Yield as a Function of Catalyst Content and Polymerization Time

g Ti/g cell.	Polyethylene yield, g PE/g cellulose					
	30 sec	60 sec	200 sec	500 sec	1000 sec	3600 sec
$1.4 \times 10^{-4}$	0.000	0.005	0.010	0.020	0.025	0.060
$2.8 \times 10^{-4}$	0.015	0.015	0.015	0.025	0.030	0.055
$4.2 \times 10^{-4}$	0.015	0.025	0.040	0.055	0.070	0.100
$8.4 \times 10^{-4}$	0.020	0.050	0.140	0.140	0.285	0.645

Exposure to olefin monomer, with or without solvent present, results in polymerization of the olefin within the paper matrix.

## EXPERIMENTAL

Since Ziegler-Natta catalysts react with water and oxygen, care had to be taken to avoid the presence of these compounds in the polymerization system. Thus, **Schleicher Schuell filter paper No. 595** was dried at 105°C in vacuo for 1 hr, **isopentane** (Baker grade) and **heptane** (Eastman-Kodak, highest purity) were dried over CaCl<sub>2</sub>, degassed by boiling, and stored over freshly extruded sodium wire. TiCl<sub>4</sub> (purified, Fisher Scientific), Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> (10% solution in *n*-heptane from Texas Alkyls), and **ethylene** (Research grade, Matheson Canada) were used without further purification.

Polymerization experiments were performed in a dry box filled with nitrogen which was continuously purged of oxygen and moisture.

A sheet of paper was dipped in 10<sup>-2</sup>*M* solution of TiCl<sub>4</sub> in isopentane and removed immediately; most isopentane evaporated in 25–30 sec. The sheet was then brought in contact with a 0.02*M* solution of Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> in *n*-heptane, where almost instantaneous reduction of TiCl<sub>4</sub> to a Ziegler-Natta catalyst occurred.

The sheet was then placed into another 0.02*M* Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> solution in *n*-heptane through which the ethylene was bubbled. Depending on the polymerization time, quantities of polyethylene varying from 0.5% to 64.5% "add-on" based on the dry weight of the paper was achieved, as recorded in Table I. The paper samples were subsequently washed with HCl and NH<sub>3</sub> solutions in methanol in order to hydrolyze the catalyst. It was later found that the same apparent effect could be achieved by washing the samples in boiling water. It is to be noted that the goal of the washing procedure is to eliminate the brownish color of the catalyst rather than to remove it from the polymer.

## RESULTS AND DISCUSSION

### Morphology of Encapsulated Paper

Since the time of contact between TiCl<sub>4</sub> and cellulose was very short, we do not believe that an appreciable amount of TiCl<sub>4</sub> has reacted with cellu-

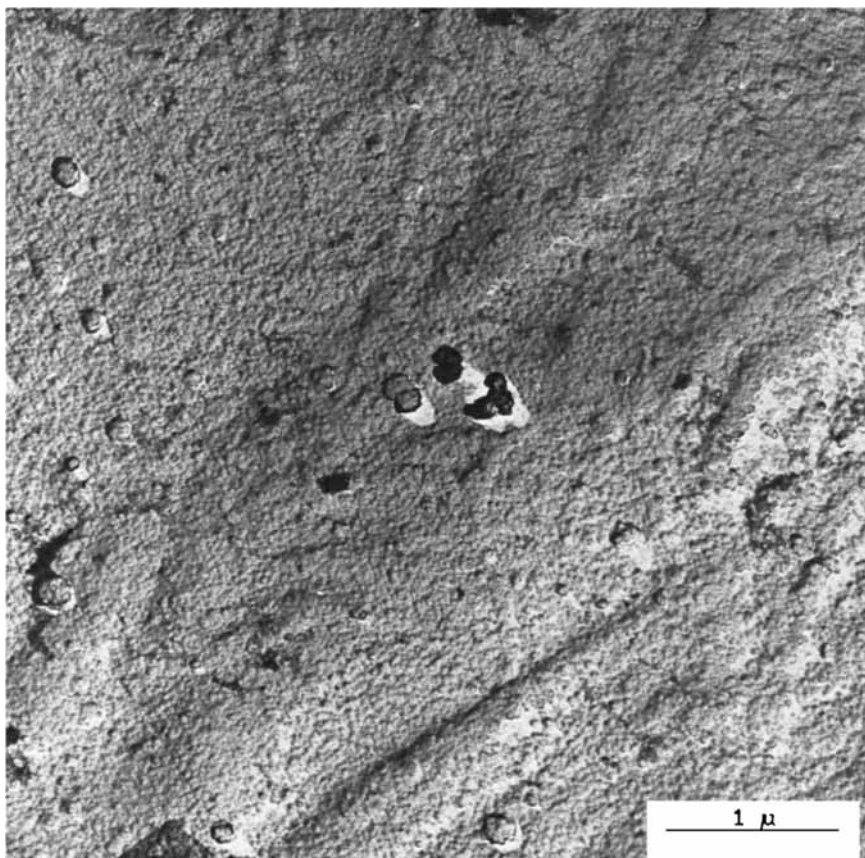


Fig. 1. Surface of a typical fiber coated with catalyst after polymerization of 15 sec (transmission electron micrograph of a carbon replica).

lose forming partial titanium alkoxides as observed in case of longer contact time.<sup>5,11</sup> This seems to be confirmed by the transmission electron micrographs of the fiber surface replicas after the catalyst has been deposited. Very small (100–500 Å), ill-defined discrete particles, some of them forming larger aggregates ( $\sim 3000$  Å), cover the fiber surface. After a short polymerization, these particles increase in dimensions, as seen in Figure 1. The mechanism of formation of polymer particles during heterogeneous Ziegler-Natta polymerization has recently been discussed elsewhere.<sup>12</sup>

Figure 2 shows the texture of the paper encapsulated with 1.6% of polyethylene (PE), as seen in the scanning electron microscope. No polyethylene is seen at this magnification. On the other hand, a paper sheet containing 5 g PE/100 g cellulose (1 min of polymerization) exhibits a much larger quantity of polymer which is attached in the form of overgrowths to the fiber surface (Fig. 3). After one hour of polymerization, the weight of paper had increased by 65% and the overgrowths completely mask the paper texture (Fig. 4). Polyethylene on the surface is present

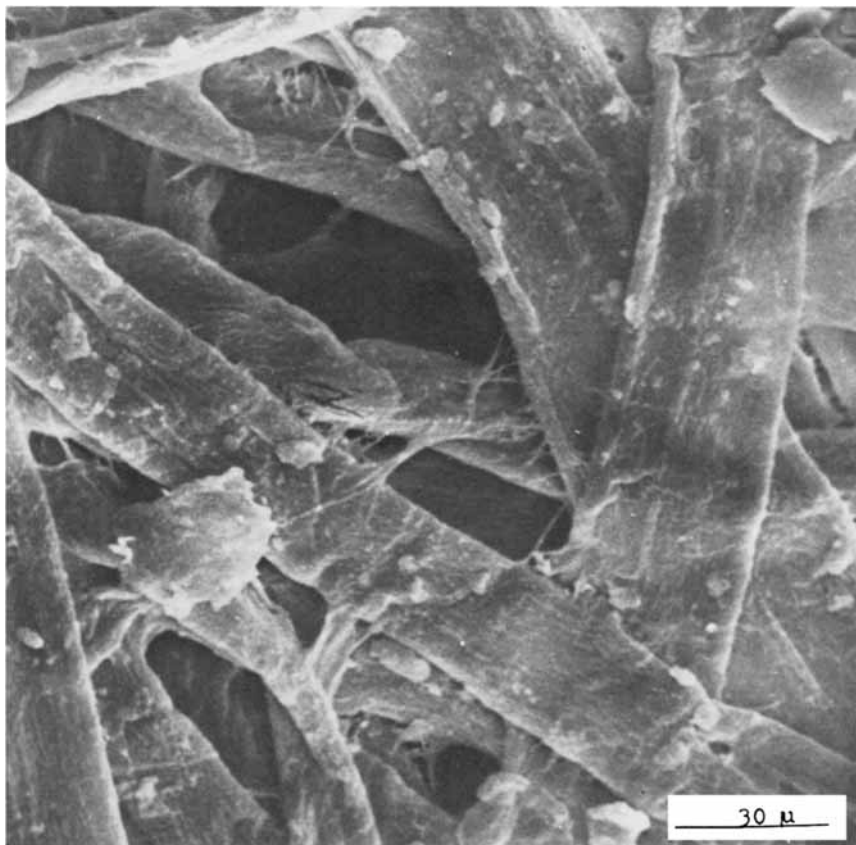


Fig. 2. Paper containing 1.6 g PE/100 cellulose (scanning electron micrograph).

as a porous film composed of little spheres having a diameter of about 1 micron.

Cellulose of the encapsulate can be dissolved in sulfuric acid and a microporous polyethylene membrane obtained. Closer examination of this membrane (Fig. 5) shows that the polymer keeps the paper-like texture after the cellulose has been removed, providing a replica of the original sheet. It is to be noted that what we see in Figure 5 is in fact only one layer of the polyethylene matrix. The sheet is around 200 microns thick, which is much more than the depth of field of the microscope used. Hence, changing the focus would result in revealing a similar picture of the same area in different layers. This shows that a considerable part of the polymer is located inside the paper matrix.

### General Properties

The encapsulated paper is hydrophobic even for the lowest polyethylene content (1.6%). Contact angle of deionized water on the paper encapsu-

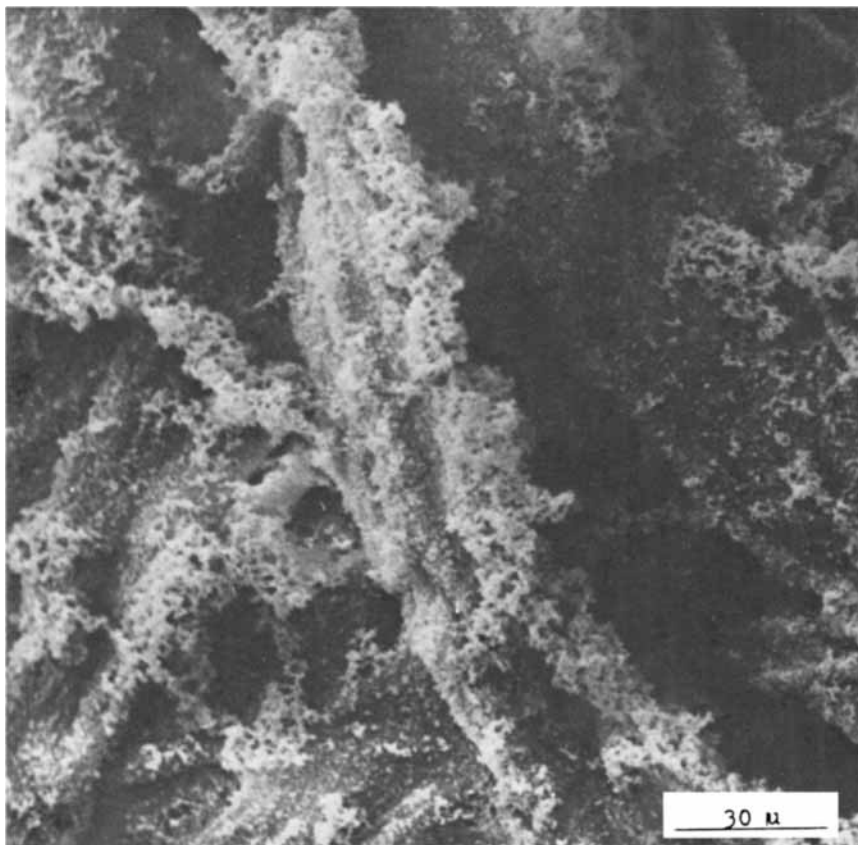


Fig. 3. Paper containing 5 g PE/100 g cellulose (scanning electron micrograph).

lated with 10% PE was found to be  $105 \pm 3^\circ$ , compared to  $107 \pm 3^\circ$  found for high-density polyethylene fibers. While the encapsulated paper is water repellent, it readily absorbs liquids with surface tensions lower than the critical surface tension of polyethylene<sup>13</sup> such as alcohols, hydrocarbons, and others.

The hand of encapsulated paper changes with polyethylene content. There does not seem to be any marked difference for the low PE contents (up to 5%) compared to the original paper, while the hand of the paper containing more than 10% of PE is suggestive of a very fine powder such as silica or powdery polyethylene.

### Mechanical Properties

The results of standard paper tests are included in Table II and can be summarized as follows: (a) Breaking load and breaking elongation increase considerably with polyethylene content, while the breaking length remains approximately constant. (b) Polyethylene residue (after extraction of cellulose with sulfuric acid) has very low tensile strength. (c)

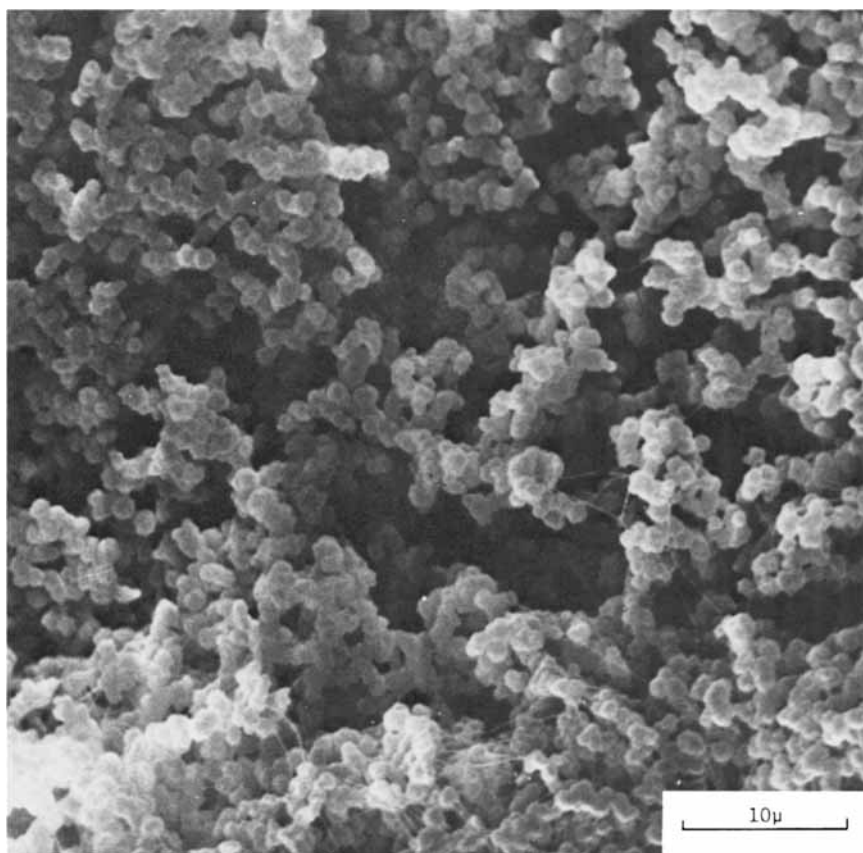


Fig. 4. Appearance of paper surface after 65 g PE/100 g cellulose has polymerized (scanning electron micrograph.)

Zero span breaking load remains constant, no matter what the “add-on” of polyethylene. (d) The stress-strain curves of a sample containing 27% “add-on” of polyethylene and of the original are almost identical at low elongations and only diverge when the elongation of the original is near the breaking point (Fig. 6). (e) Toughness index (area under the stress-strain curve) and fold resistance increase with polyethylene content. Tear resistance also increases although only slightly.

The paper matrix is thus reinforced by introduction of a complementary matrix of polyethylene. The data of Table II cannot be explained by a simple addition of the properties of untreated paper plus those of the polyethylene matrix, since the mechanical properties of the latter are much lower than the reinforcement observed.

According to Rance,<sup>14</sup> the tensile behavior of the paper can be attributed to a combination of elastic behavior of the fibrous components, a progressive breaking of interfibrillar bonds, and a frictional drag as the fibrous elements slide over one another after bond breaking. Since the results

TABLE II  
Properties of Encapsulated Paper as a Function of Polyethylene Content

	0 <sup>a</sup>	1.65	3.05	3.5	4.4	16.7	22.5	27.6
g PE/100 g cell								
Basis weight, g/m <sup>2</sup>	66.4	67.5	68.4	68.7	69.3	77.4	81.3	84.5
Caliper, mm/sheet	0.177(4)	0.188(4)	0.189(5)	0.189(4)	0.191(3)	0.200(7)	0.210(9)	0.236(17)
Bulking thickness, mm/5 sheets	0.840(15)	0.865(15)	0.855(10)	0.890(5)	0.910(5)	0.940(10)	0.985(20)	1.060(20)
Breaking load, kg	3.57(15)	3.55(5)	3.45(22)	3.65(14)	3.77(14)	4.31(24)	4.39(5)	4.55(12)
Breaking elongation, %	2.09(14)	2.22(10)	2.29(6)	2.36(15)	2.51(15)	2.83(17)	3.17(17)	3.26(10)
Breaking length, km	3.58(15)	3.51(5)	3.39(21)	3.54(13)	3.63(13)	3.71(21)	3.60(4)	3.59(9)
Zero span B.L., km	10.4(3)	10.1(4)	9.2(4)	9.8(7)	9.6(3)	9.1(3)	8.5(3)	8.1(6)
Wet strength, kg	0.57	—	1.35	—	1.51	2.22	—	2.25
Breaking strength of PE residue, g		0	0	0	0	~20	~20	~30
Toughness index, g·cm	512(69)	582(41)	557(25)	601(5)	609(79)	867(77)	966(39)	1051(60)
Tear factor	102	93	105	105	105	119	121	119
Double folds, MIT	29(6)	19(4)	21(6)	11(6)	15(7)	93(49)	106(35)	116(26)
Air resistance, sec/100 cm <sup>2</sup>	1.1(2)	1.3(2)	2.4(7)	2.6(10)	2.5(3)	8.1(25)	16.9(40)	17.9(71)

<sup>a</sup> Polyethylene content, g PE/100 g cellulose.





Fig. 5. Polyethylene residue after extraction of cellulose as seen in optical microscope under crossed polarizers.

of the zero-span test show that the presence of polyethylene within the paper matrix does not modify the ultimate strength of the fibers themselves, the explanation for the reinforcement has to be sought in the reinforcement of interfibrillar bonds due to additional adhesion created by the polyethylene. Furthermore, frictional properties between fibers are probably changed due to the nascent morphology of the polyethylene.<sup>12</sup>

While the tensile strength of the original paper, measured with the sample immersed in water (for 90 sec prior to the experiment in this case), is ap-

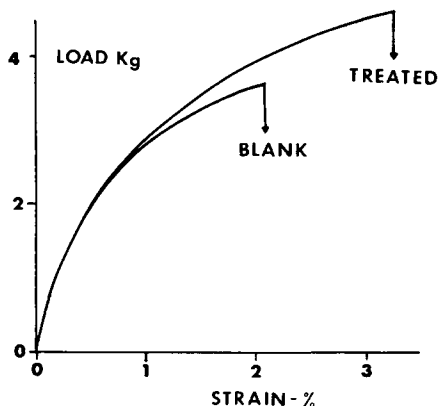


Fig. 6. Stress-strain curves of untreated (blank) paper and paper treated with 27 g PE/100 g cellulose. The load in kg is marked on the ordinate.

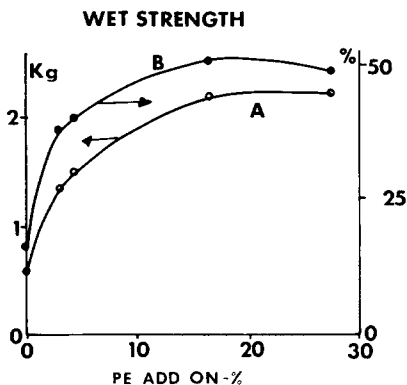


Fig. 7. Breaking strength of paper immersed in water for 90 sec prior to and during testing: (A) breaking load in kg (left ordinate); (B) breaking strength in % of dry breaking strength (right ordinate).

proximately 15% of that measured in air at 50% R.H., the strength retention is considerably greater for encapsulated paper and attains 50% at a polyethylene content of about 15% (Fig. 7). It would appear that the interfibrillar bonds are at least partially protected by polyethylene.

Variation of thickness as a function of polyethylene content (Fig. 8) shows that in the first stages of the polymerization, more polymer is formed at the paper surface than in its interior. This is easily understood since the paper which is being put in the monomer solution is soaked with  $\text{Al}(\text{C}_2\text{H}_5)_3$  solution and the monomer has to diffuse to the interior while the surface is immediately accessible to polymerization. This initial period is followed by another one during which increase of thickness is only moderate, indicating polymer formation within the paper sheet. The final increase of thickness is no doubt due to the expansion of the paper matrix filled with polymer.

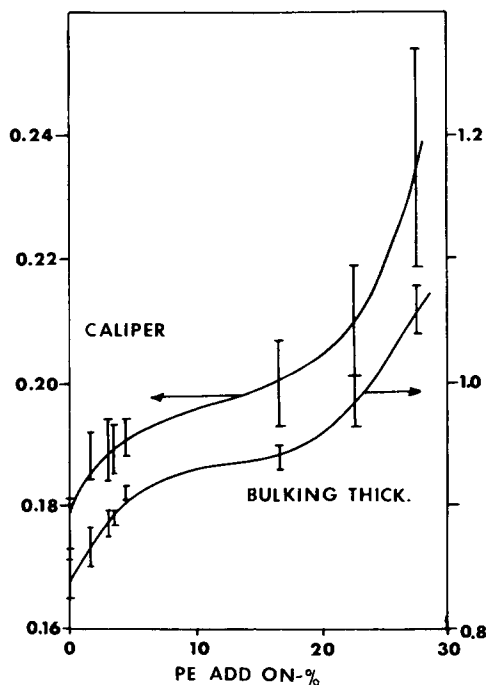


Fig. 8. Caliper (mm/sheet) (left ordinate) and bulking thickness (mm/5 sheets) (right ordinate) of the encapsulated paper as a function of PE content.

As it was expected, air resistance of encapsulated paper increases with the polyethylene content, because of the filling of interfiber space with polymer.

### Optical Properties

There is a significant increase in opacity due to the presence of polyethylene in the paper matrix (Fig. 9). As seen in Figure 4, polymerized polyethylene is composed of little spheres whose diameters are similar to the wavelengths of visible light which is an ideal situation for scattering and reflection of light in the composite system.

Brightness and visual efficiency of encapsulated paper also increase with polyethylene content, though there is a slight decrease in these properties as one proceeds from the original paper to that with the lowest PE content (1.6%). It would seem that the catalyst, which is brown colored, could not be entirely eliminated during the washing operations.

### CONCLUSIONS

The synthesis of a microporous polyethylene web whose gross morphology is complementary to that of paper has been achieved. The basic principles involved in its preparation are as follows: (a) The polymerization catalyst

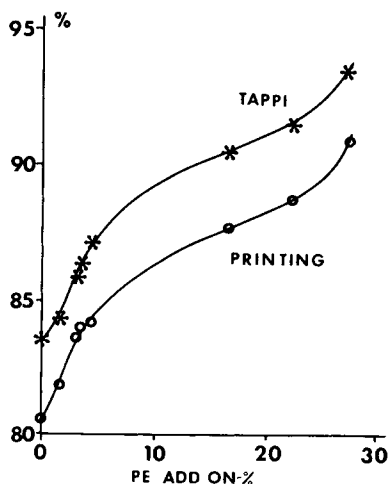


Fig. 9. Opacity (%) of the encapsulated paper as a function of PE content.

is rapidly carried to the interfiber spaces of the paper matrix and deposited there as a heterogeneous precipitate. (b) A heterogeneous polymerization is triggered by the presence of monomer whose polymer is insoluble in the reaction medium.

Since the interfiber spaces of the cellulose matrix are interconnected, it follows that the solid polymer which is generated therein will be a continuous matrix whose spatial distribution will be complementary to that of the cellulosic fiber construct. This is in agreement with the results of the work on nascent polyethylene films formed on  $VCl_3/Al(C_2H_5)_3$  catalyst deposited on glass.<sup>15,16</sup> In this case, the substrate side of the film is a continuous flat replica of the substrate, while the exterior exhibits structures similar to those shown here. Nascent polymer present within the paper matrix is the most important feature of the present study. In the present case, conditions were chosen to yield a particulate product whose light-scattering properties had a favorable effect on the paper opacity.

The detailed work on filter paper encapsulation has been followed up with studies on a wide variety of paper sheets: from unbleached groundwood to rag paper. Each paper type demands its own special conditions but there is no limitations on encapsulation due to the paper itself. An important economic feature in attempting to develop a continuous encapsulation of the type here described is the speed of polymerization. No attempt has been made to optimize this.

Several fibrous systems other than paper were studied. Among these were nonwovens and felts as well as a standard cotton greige fabric. In all cases, the results were similar to what was found for paper but with variations which were explainable in terms of the fabric construction particularly as regards bulkiness. It is clear that textile fabrics which present two peaks in their pore size distribution curve—interfiber spaces

within the twisted yarn and interyarn spaces between the warp and fill—will require a somewhat different approach than fiber matrices with a single peak in the interfiber spaces. So far, there does not seem to be evidence that catalyst deposited as we have described in this study generates polyethylene inside the cellulosic fibers.

Although the effect of the “aftertreatments” of the encapsulated paper on properties has not been systematically studied, preliminary experiments have shown that the treated paper can be texturized by heat and pressure. Surface properties such as smoothness and gloss are significantly modified.

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