Preferred citation: H. Mark. Web formation with synthetic organic polymers. In Consolidation of the Paper Web, *Trans. of the IIIrd Fund. Res. Symp. Cambridge, 1965*, (F. Bolam, ed.), pp 38–56, FRC, Manchester, 2018. DOI: 10.15376/frc.1965.1.38.

WEB FORMATION WITH SYNTHETIC ORGANIC POLYMERS

H. MARK, Polytechnic Institute of Brooklyn, New York

Synopsis—Organic polymers have always been useful for the making of fibres, films, rubbers, plastics, adhesives and coatings and cover a wide range of properties. For several years, systematic efforts have been made to explore the use of fully synthetic fibres on a papermachine either alone or together with cellulose materials. Several sheet properties can be substantially improved by this approach. More recently, the preparation of polymer systems has been studied that occupy an intermediate position between a uniform fibre and a homogeneous film. They have been called 'fibrids' and permit one to prepare two-dimensional sheet-like entities without the use of a liquid vehicle (such as water on a papermachine) that range in their properties from paper to textiles.

Introduction

THE essential conditions for the classical web formation on a papermachine can be briefly summarised as follows—

- 1. The stock must consist of hygroscopic fibres to ensure easy formation of a stable suspension in water at consistencies between 0.5 and 2.0 per cent.
- 2. The fibres must be able to fibrillate through mechanical action with an increase of their accessible surface by a factor between 50 and 200.
- 3. The length (2-10 mm), diameter (10-20 microns) and flexibility of the fibres in the hydrated state must be such that they entangle and establish local contact with each other at the crossover points.
- 4. The fibres must carry groups that can develop intermolecular forces if brought in sufficiently close contact with each other: 3.5-4.5 Å for dipole bonds, 2.5-3.0 Å for hydrogen bonds.

In the head box, the weight ratio of water to fibre is about 100 to 1; after suction treatment, it is about 4:1; at entry into the dryer section, it approaches 1:1 and, in the final sheet, it is about 0.07:1. The consolidation should take place at linear web speeds above 450 ft/min (it is sometimes as high as 2 000 ft/min) and should be as uniform as possible across the sheet.

Many man-spun and man-made polymers can be brought into a state in which they satisfy the above conditions either alone or in mixtures with each

Polymer web formation

other and/or with natural cellulose materials. This represents *one* interesting approach to the formation of papers and non-woven fabrics from synthetics: the other stems from the possibility of eliminating water completely as a carrier for the stock and to lay down a random web from substantially linear fibrous elements or strands immediately after their formation from a solution or from the melt in analogy to the dry and melt spinning of yarns or staple fibres and to the casting of continuous films.

This paper intends to give a brief account of the materials and methods that are at present used in both approaches, of the sheet properties obtained and of the actual and potential uses of the various products.

Rayon fibres

VISCOSE RAYON staple, in all its present existing varieties, offers a number of advantages as a candidate for web formation on a papermachine alone or with other cellulosics or synthetics—

- 1. They are hydrophilic and form readily stable slurries of adequate consistency.
- 2. They can be easily produced with good control of length, cross-section, strength, elongation, uniformity, whiteness and covering power.
- 3. They cost less than any other synthetic organic or metallic fibre (28–35 cents/ lb).

Power beating or other equivalent mechanical treatment of standard rayon types does not produce sufficient fibrillation and hydration of the filaments to render the stock self-bonding on existing papermachines. It is necessary therefore to take special steps and to produce web-forming types of viscose rayon fibre or fibre compositions.

One way to achieve this goal is to spin multi-cellular, compartmented filaments that contain pores of controlled average volume and with controlled average wall thickness. A well-known representative of such a foamed cellulose filament is the self-bonding RD-101 fibre of the American Viscose Division of FMC, which is capable of forming strong and tough webs alone, also in co-operation with natural cellulosics or other fibres.

Table 1 shows the dependence of the mechanical properties of a RD-101 web as a function of fibre length and reveals that tensile strength is essentially constant (at about 2 600 m) until $\frac{3}{8}$ in, tearing strength increases with length up to 240 at $\frac{5}{8}$ in and Mullen bursting strength has a flat maximum between $\frac{1}{4}$ in and $\frac{1}{2}$ in.

Table 2 gives corresponding figures for the effect of filament diameter and discloses a relatively pronounced maximum for tensile and bursting strengths near 6 denier and a monotonous decrease of tearing strength from 1 denier (250) to 12 denier (90).

 TABLE 1—TENSILE STRENGTH, TEAR FACTOR AND BURST FACTOR OF RD-101 WEBS AS FUNCTIONS OF FIBRE LENGTH

Fibre length, in	Tensile strength, m	Tear factor*	Burst factor†
	2 600	80	15
	2 600	180	27
	2 500	215	29
	2 300	230	25
	1 500	240	18

* Tear factor = $(71.7 \times \text{Elmendorf tear in g})$ for TAPPI ream weight † Burst factor = $(50 \times \text{Mullen burst in lb/in}^2)$ for TAPPI ream weight

TAPPI substance = weight in 1b of 500 sheets each 25 in \times 40 in. See, for example, Technical Service Bulletins S-12 and S-13 of American Viscose Division of FMC and O. A. Battista, *Synthetic fibres in papermaking* (Interscience, New York, 1960), 16–22

Table 3 presents figures referring to blends of bleached kraft pulp with RD-101 fibre and demonstrates that the addition of 5 per cent RD-101 has a favourable influence on the mechanical properties of the sheet, although it must be admitted that the effect is not overwhelming and, in view of the cost of the additive, probably not of great economic significance.

Fibre diameter, denier	Tensile strength, m	Tear factor*	Burst factor
1	1 200	250	10
3	1 700	240	12
6	2 000	170	14
9	1 000	140	6
12	1 000	90	5

TABLE 2-TENSILE STRENGTH, TEAR FACTOR AND BURST FACTOR OF **RD-101 WEBS AS FUNCTIONS OF THE FIBRE DIAMETER**

*. † See Table 1

Another way to prepare a web-forming viscose rayon staple fibre capitalises on the use of fibrillatable rayon filaments, which can be beaten alone or with other fibres to give highly hydrating web-forming systems. Normal viscose rayon with an average DP of 350-400 cannot be successfully fibril-

TABLE 3-SOME PHYSICAL PROPERTIES OF BLENDED PAPER SHEET CONTAINING BLEACHED KRAFT PULP (BKP) AND FIBRE RD-101

Content of BKP, per cent	100	95	90	0
Content of RD-101, per cent	0	5	10	100
Tensile strength*	4 400	4 750	4 450	3 500
Burst factor†	40	43	43	46
Tear factor*	190	210	195	180

*, † See Table 1 for references

lated, but it was found that controlled chemical degradation through hydrolysis leads to readily fibrillatable materials; this is shown in Table 4, which discloses that, in the aproximate DP range of 120–200, fibrillatable rayons can be obtained to give favourable web and sheet properties.

Hydrolysis treatment with 10 per cent sulphuric acid	Average DP	Fibrillation after beating
None	370	None
12 min at 65°C	290	Very poor
20 min at 65°C	220	Good
10 min at 80°C	160	Excellent
10 min at 85°C	130	Excellent
20 min at 75°C	50	Powder; no fibri

TABLE 4—INFLUENCE OF DP ON THE FIBRILLATING CHARACTER OF VISCOSE RAYON FILAMENTS*

* See, for example, H. E. Shearer, B.P. 687 041 (1953); O. A. Battista, U.S.P. 3 052 593 (1962);
 O. A. Battista, Synthetic fibres in papermaking (Interscience, New York, 1960), 21–29

A less conventional but much more spectacular way to produce fibrillatable rayons and, in fact, many other fibrillatable filaments makes use of the socalled *hybrid* (bi-component or conjugate) fibres. They are spun from a multihole spinneret, which is so constructed that each hole is supplied with two independent streams of solution or melt. These two liquids mix only incompletely and the resulting fibre consists of two distinctly separated parts that stick together along their interface more or less tenaciously. Fig. 1 shows a length section of a single spinneret hole of this type in which the two polymeric liquids A and B enter the countersink on the two sides of a dividing plate P and can diffuse into each other only to a limited extent while they pass through the capillary of the spinneret. If one wants a relatively firm connection between the two components, one lifts the dividing plate; if one wants to obtain easily separable systems, one pushes it further down into the spinneret hole.

This technique is rather old and has been used for quite a few years to cospin viscose solutions of different degrees of ripening or containing different pigments and it is now used with great success to produce hybrid filaments containing almost any kind of combination of different polymers spun from solution or from the melt.* If one aims at fibrillatable filaments, the adhesion between the two components must not be too high so that one can obtain a system of very fine fibrils (down to 150 Å diameter) by chemical treatment and beating of hybrid fibres, one half of which consist of

^{*} Particularly successful hybrid fibres for tensile use are Sayelle Orlon 21 and Cantrece nylon

regenerated cellulose, the other half formed by the cospinning of another alkali-soluble polymer such as hydroxyethyl, hydroxypropyl, carboxymethyl or carboxyethyl cellulose, also of amylopectin, polyvinyl alcohol, polyacrylic acid or various other acrylic copolymers. Together with the degree of interlocking of the two components, one can also vary their weight proportion and even their relative geometric arrangement over the cross-section Once the spinnerets are made and conditions for a given system have been worked



out, hybrid fibre spinning is not more difficult and expensive than the production of a simple commercial fibre.

Table 5 gives an idea of the web-forming capacity of several hybrid fibres that contained about 50 per cent of regenerated cellulose and shows that reasonable values of tensile, tearing and bursting strengths are obtained, although none of them could compete with a good bleached kraft paper.

Another method of producing cellulose webs with acceptable properties uses self-bonding hydrophilic fibres that are either used alone or added to a

Fibre	Tensile	Tear	Burst
composition	strength, m	factor	factor
50% C; 50% HEC	2 350	93	13
50% C; 50% Am	1 040	126	18
50% C; 48% MC	2 630	52	31
75% C; 25% PAA	2 000	300	14

TABLE 5-WEB-FORMING CAPACITY OF FIBRILLATED HYBRID FIBRES

C = Regenerated cellulose HEC = Hydroxyethyl cellulose MC = Methyl cellulose Am = Amylopectin PAA = Polyacrylic acid

stock of rayon staple in desired proportions. One representative of this type is fibre 776 of American Viscose, which consists of a hydrophilic cellulose ether such as hydroxypropyl or carboxyethyl cellulose with degrees of substitution ranging 5–10 per cent.

Table 6 shows that quite respectable mechanical properties can be obtained if such fibres are used as binders in amounts of 5–10 per cent on the viscose rayon fibres.

TABLE 6—PROPERTIES OF VISCOSE RAYON SHEET BONDED WITH 6 PER CENT OF CARBOXYETHYLCELLULOSE FIBRE

pH value of	Tensile strength,	Tear	Burst	Elongation
system	m	factor	factor	to break
4.4 6.4 8.2 8.7	2 930 3 630 3 630 3 630 3 630	200 170 100 90	20 30 30 30 30	3.1 4.0 3.5 3.5

Instead of hydrophilic natural or synthetic polymers, one can also use powdered and fibrous olefin polymers to produce a coherent web of viscose rayon fibres. In this case, the bonding is produced by moulding the thermoplastic fibres of the binder on to, around and between the viscous rayon filaments. Low density and high density polyethylene, polypropylene and copolymers of ethylene with polar monomers (EVA, EMA and Surlyn) are used and, according to the plastic nature of the binder, calendering temperatures of 350°–400°F are used for 20–26 sec at pressures ranging 250– 350 lbf/in². The best results are obtained with fibrous binders, particularly if anchoring or cementing agents are used, which strengthen the bonds at the crossover points of the hydrophilic rayon filaments and the essentially hydrophobic polyolefin fibres. Such anchoring agents are water dispersible, preferably somewhat cationic, medium molecular weight compositions, which

are added to the beater, relatively adsorbed by the cellulose and which comould with the polyolefin at elevated temperatures, because of the nonpolar chain elements that they contain. One family of anchoring agents are the Accobonds, made of urea- or melamine-formaldehyde condensation products, others are polyethyleneimines or ethyleneimine-propyleneoxide copolymers and more recent types are prepared from polyamide-amine or polyalkylene polyamine resins, which also can contain amide, ether or ester bonds. All anchoring agents of the latter type can be cross-linked and cured on the web with epichlorohydrin or other polyfunctional epoxy compounds (Epons, Araldites, etc.), which increases the mechanical properties particularly in the wet state.

TABLE 7—SOME MECHANICAL PROPERTIES OF RXL-RAYON STAPLE SHEETS BONDED WITH DIFFERENT POLYOLEFIN BINDERS IN THE PRESENCE OF DIFFERENT ANCHORING AGENTS

Binder (35 per cent)	Anchoring agent	Tensile strength, m	Tearing strength, g	Bursting strength, kg × 10 ⁻⁴
Polyethylene A	Melamine-formaldehyde	5 200	180	2 900
Polypropylene	Polyethyleneimine	3 800	280	1 100
Polyethylene B	Polyethyleneimine	4 900	220	2 300

Polyethylene A has a low carbonyl content Polyethylene B has a relatively high carbonyl content

Table 7 summarises a few data on the effect of polyolefin binders plus anchoring agents on the mechanical properties of viscose rayon fibre webs and sheet and illustrates the fact that under certain conditions relatively high values of the most important properties-tensile, tear and burst-can be obtained. It should not be forgotten, however, that any improvement over the best bleached kraft papers is achieved only on the basis of substantially higher costs and such materials as polyolefin-bonded viscose rayon sheets can be considered only as interesting fundamental information on the principles of web formation and consolidation. Their practical value will probably remain restricted to the production of speciality items of relatively small sales volume. We shall see later that new web and sheet formers based entirely or almost entirely on inexpensive olefin polymers represent a much more serious threat to large volume products, which hitherto have been exclusively made from natural cellulose materials.

Fibres of vinyl and acrylic polymers

IT WILL be not surprising that the same principles enumerated for viscose rayon are applicable also for all fully synthetic fibres, with certain variations concerning importance and mode of operation.

Polymer web formation

Polyvinyl alcohol (PVA) is most closely related to cellulose materials in its hydration characteristics and its fibre-to-fibre bonding capacity, owing to the large number of hydroxyl groups that the polymer chains carry along a given length. PVA staple can be readily spun from aqueous solutions of the polymer and highly oriented by a stretching or drawing process with ratios between 4 and 6 to 1: the filaments can be fibrillated to a certain extent by beating, if the molecular weight of the pure polymer is not too high. They hydrate in the fibrillated state and have self-bonding properties that permit web formation on a papermachine either alone or in conjunction with other filaments, though the final sheets have to be treated with a cross-linking agent (formaldehvde or preferable bi-functional methyl compounds or water dispersible capped di-isocvanates) to render them sufficiently resistant to swelling and dissolution in water. Papers of this type, consisting of PVA alone or together with woodpulp, are already used on a commercial scale in Japan, where the economic conditions for the production of PVA are particularly favourable: they excel by their tensile strength (above 4 500 m), tear factor (above 300) and burst factor (above 60*) and show satisfactory behaviour in other important properties such as wet strength, covering power, mildew resistance and printability.

An almost unlimited selection exists of copolymers of vinylalcohol with other simple ethylene compounds (ethylene propylene, vinylchloride, styrene, acrylonitrile and others) that permits control of the intrinsic hydrophilic character and fibrillability of fibres with 1.5–3.0 denier and $\frac{1}{8}-\frac{1}{2}$ in length and it is very probable that one can look forward to substantial progress in this branch of papermaking with synthetic fibres. It is evident that all products of this kind will be of substantially higher cost than woodpulp-based papers and will probably capture uses only in speciality fields.

Interesting progress has been made and is to be expected in the web formation of acrylic copolymers with acrylonitrile as a major component (because of its contribution to high softening, hydrophobility, solvent resistance, outdoor stability and superior electrical performance) and with vinylchloride, vinylacetate, acrylic acid, methylolacrylamide and many other ethylene compounds as property controlling comonomers.

It was found, for instance, that many staple fibres of acrylic copolymers can be fibrillated and made self-bonding by beating in warm water,[†] producing webs of outstanding wet strength characteristics (more than 50 per cent of the dry strength) that can be substantially improved by hot calendering

^{*} The corresponding values for a high grade bleached kraft paper are tensile strength 4 400 m, tear factor 200 and burst factor 40

² See, for example, Brown, B. J., *Proc. J. Text. Inst.*, 1962, **53**, 682, U.S. Patent 2 810 646 (1957), U.S. P.3 047 422 (1962) or Arledter, H. F., *Tappi*, 1959, **41**, 177A

TABLE 8—EFFECT OF HOT CALENDERING ON THE PROPERTIES OF ACRYLIC TYPE WEBS

Temperature, °F	72	200	220	240	
Thickness, mil	7.5	6.5	60	6.0	
Tensile strength, g/in	7 800	10 300	14 500	18 800	
Mullen bursting strength, lb/in ²	21	40	48	59	

(see Table 8) and by the use of resinous binders (see Table 9) such as solutions or emulsions of polyethyleneimine, ethyleneimine-propylene oxide copolymers, polyalkylene polyamines and similar compositions that are cured on the fibres with the aid of epichlorohydrin or similar polyfunctional compounds.

TABLE 9-EFFECT OF BINDER ADDITION ON THE PROPERTIES OF ACRYLIC TYPE WEBS

Percentage of binder added	2	6
Thickness, mil	15	16
Tensile strength, g/in	13 500	16 000
Wet tensile strength, g/in	7 000	8 000
Mullen bursting strength, lb/in ²	30	40

Hybrid fibres of a hydrophobic and hydrophilic copolymer at ratios around 1:1 have already established a prominent position in textile uses (Sayelle Orlon 21) and provide valuable 'know-how' for the preparation of corresponding compositions endowed with specifically web-forming properties.

TABLE 10—PERCENTAGE STRENGTH RETENTION OF ACRYLIC TYPE WEBS AFTER 150 h AT $120\,^{\circ}\mathrm{F}$

Exposure to	Percentage retention
Water	90
30 per cent sulphuric acid	85
10 per cent hydrochloric acid	90
10 per cent nitric acid	85
10 per cent sodium hydroxide	87
3 per cent hydrogen peroxide	75

One special attribute of acrylic fibre type webs and sheets is their durability to outdoor exposure and to the action of chemicals, moulds and ultraviolet light. Table 10 presents some information on this behaviour. Another field of preferred application for polyacrylic webs is favoured by their

TABLE 11—PROPERTIES OF ACRYLIC TYPE WEBS IMPREGNATED WITH ABOUT 50 PER CENT PHENOL-FORMALDEHYDE RESIN

Moisture absorption, per cent Flexural strength, $ b n^2$ (machine-direction) Flexural strength, $ b n^2$ (cross-direction) Izod impact strength, $ft/ b $ in (machine-direction) Izod impact strength, $ft/ b $ in (cross-direction) Insulation resistance, ohms Loss factor $\times 10^6$, cycles	$\begin{array}{c} 17\ 000-25\ 000\\ 12\ 000-18\ 000\\ 1.0-2.5\\ 0.8-2.0\\ 10^{13}\\ 0.043-0.048 \end{array}$
--	--

excellent electrical performance either as such or in conjunction with thermosetting preparations such as phenol-formaldehyde or epoxy resins. Table 11 shows a few pertinent figures.

Polyamides

THE STANDARD commercial polyamide staple fibres (6 nylon, 66 nylon and 11 nylon) are not hygroscopic (their standard moisture regain ranges 2.0–3.5 per cent) and cannot be fibrillated by beating or other limited mechanical treatment. In order to form them into a web, they must either be made fibrillated by the hybrid fibre technique or have to be used with other fibres as binders, eventually with the additional aid of anchoring agents or calendering procedures.

Fibre	Binder used		Tensile	Elonga-	Tearing	Bursting
useu	Туре	Amount, per cent	lb/in	per cent	g g	lb/in ²
3 den, $\frac{3}{8}$ in 3 den, $\frac{3}{8}$ in 3 den, $\frac{1}{4}$ in Kraft (control)	Zinc bromide T-8 Fibrid 101 —	10 5 15	32 33 20 12	15 33 30 3	1 050 1 230 1 020 280	67 88 110 35

TABLE 12-SOME MECHANICAL PROPERTIES OF 100 PER CENT 66 NYLON WEBS

Best developed* are webs and sheets of nylon staple and cullulosics in which 15–25 per cent polyamide filaments (denier between 1.5 and 15, staple length between $\frac{1}{4}$ in and $\frac{3}{4}$ in) are put on a papermachine with a binder and with fibrillated woodpulp at stock densities within 0.2–1.0 and run essentially under standard conditions. Outstanding among the properties of the pure nylon and blended sheets are tensile, tearing and bursting strengths as demonstrated by the figures of Table 12. The most effective binders are zinc bromide, which acts as a softener for the polyamide fibre type 8 nylon,

* See, for example, Auspos, L. A. and Winn, E. B., Tappi, 1962, 45, 741 and U.S. Patent 3 057 772 (1962)

which is a hydrophilic polyamide and acrylic fibrid 101, which will be described in more detail later. Table 13 presents a few data on the mechanical properties of nylon-cellulose blends using different binders.

TABLE 13—SOME MECHANICAL PROPERTIES OF WEBS MADE FROM 66 NYLON AND CELLU-LOSIC BLENDS

Composition of web	Tensile strength, lb/in	Bursting strength, lb/in ²	Tearing strength, g	MIT folding endurance
40 nylon, 40 pulp, 20 acrylic	23/17	50/30	170/110	40 000/13 500
High wet strength paper	44/25	50/30	85/95	1 400/ 1 300

The properties are given in the machine/cross-directions

Present experience indicates that the use of nylon staple alone or in conjunction with woodpulp can lead to certain exceptional web and sheet properties that are, however, achieved on the basis of a rather substantial cost increase. This indicates that the use of standard nylon staple on a papermachine will not capture the large markets of the cellulose materials for packaging and printing.

Polyesters

THE MOST important polyesters for web formation are polyethyl terephthalate (Terylene, Dacron) and copolymers in which a certain percentage (10–20 per cent) of the terephthalic acid is replaced either by isophthalic acid or by hydroxybenzoic acid. Staple fibres of these polymers are strong, tough, hydrophobic (moisture regain under standard conditions around 0.5 per cent), high melting (melting points are above 220°C) and very solvent resistant; they do not hydrate and cannot be fibrillated; therefore, they are not selfbonding and have to be used either as hybrid fibres or together with an appropriate hydrophilic binder and eventually with an anchoring agent. In general, one uses similar binders and adhesives as for acrylics and nylon.*

Polyester fibres sold to the paper industry are generally ready for use without further treatment. They should be handled in a manner identical to that of nylon fibres of comparable denier and cut length. The fibres will readily disperse in water at room temperature with minimum agitation. Consistencies of 0.5–1.0 per cent are of the optimum order to avoid fibre entanglement. Since the polyester fibre stock drains so rapidly, the consistency is still further reduced to 0.05–0.1 per cent in the head box. Under these conditions, good sheet formation is possible with most standard papermaking equipment. For blends of polyester fibres with cellulose pulps, the polyester is added to the pulp in the beater or at the stock chest, if sufficient agitation is

^{*} See, for example, Auspos, L. A. and Winn, E. B., Tappi, 1962, 45, 741

available. Good sheet formation can be achieved on either Fourdrinier machine or Rotiformer.

Paper	Binder	Tensile strength, lb/in	Elonga- tion, per cent	Tearing strength, g	Bursting strength, lb/in ²	MIT folding endur- ance
Kraft paper	10º/ magnasium	12	3	280	35	1 200
$2 \operatorname{den}, \frac{1}{2} \operatorname{in}$ thiocyanate	22	8	384	132	68 000	
$\begin{array}{c} 100\% \text{ Dacron,} \\ 3 \text{ den, } \frac{1}{4} \text{ in} \end{array}$	25% 201 fibrid	46	33	680	156	

TABLE 14PROPERTIES OF PAPERS OF 100 PER CENT POLIESTER FIDE	TABLE	14PROPERTIES	OF	PAPERS	OF	100	PER	CENT	POLYESTER	FIBRE
---	-------	--------------	----	--------	----	-----	-----	------	-----------	-------

The properties of 100 per cent polyester fibre webs are strongly dependent on the binder, which is clearly shown in Table 14. These papers are almost as strong as those of nylon and actually compare favourably with nylon in most physical properties. The elongation is lower, which is a direct reflection of the lower elongation of the fibre.

In addition to being about equal to nylon in most physical and mechanical properties, papers of 100 per cent polyester fibre have several important advantages. Perhaps the most outstanding is their low moisture absorption, which is reflected in superior wet strengths and dimensional stability (illustrated in Table 15).

TABLE 15—DRY AND WET STRENGTHS OF SY	INTHETIC FIBRE PAPERS
--------------------------------------	-----------------------

Paper	Binder	Ter strengt	nsile h,*lb/in	Ratio Wat/Dry
		Dry	Wet	
Kraft High wet strength map paper Nylon, 3 den, $\frac{1}{4}$ in Polyester fibre, 3 den, $\frac{1}{4}$ in		25 35 51 46	2 13 28 42	0.08 0.37 0.55 0.91

* Average of machine- and cross-directions

Papers of 100 per cent Dacron polyester fibre bonded with polyester fibrid 201 retain 91 per cent of their dry strength when wet at room temperature, whereas nylon paper bonded with polyamide fibrid 101 retains only 55 per cent of its dry strength. This is obviously orders of magnitude better than cellulose papers (8 per cent retention of dry strength when wet), even if treated with a good wet strength resin (37 per cent retention). These high values of wet strength are also a reflection of the excellent bonding of the fibres by the synthetic polymers (fibrids). It was found, too, that papers containing polyester

fibres, specifically textryls of Dacron, are extremely stable to changes in relative humidity compared with kraft or nylon papers. The dimensional stability of polyester fibre paper is useful in maps, apparel interlinings, electrical insulation, computer tapes and tracing paper.

The resistance of polyester fibres to attack by certain chemicals is carried over into paper. With an equally resistant binder, papers of polyester fibres are unaffected by solutions of many common acids. For example, a Dacron paper composed of 75 per cent 3 denier, $\frac{1}{4}$ in Dacron and 25 per cent polyester fibrid 201 showed no loss in tensile strength after exposure for one week at 122°F to 10 per cent solutions of hydrochloric acid, nitric acid or hydrogen peroxide. On the other hand, it was disintegrated completely by similar exposure to a 10 per cent solution hydroxide solution.

Paper	Tensile strength, lb/in	Tearing strength, g	Folding endurance, cycles	Expansivity per 15% rh change, percentage of maximum
High wet strength map	44/25	85/94	1 410/1 300	0.07/0.21
40% Dacron/40% rag/ 20% acrylic binder	27/22	151/14	14 300/11 300	0.06/0.10
20% acrylic binder	23/17	168/108	40 000/13 500	0.20/0.28

TABLE 16-PROPERTIES OF POLYESTER AND WOODPULP BLEND PAPERS

Another important property of polyester webs is their excellent electrical characteristics, which have made Mylar (a polyester film) and several types of polyester paper* almost indispensable for many electronic circuits.

Polyester fibres are used in blends with cellulose materials almost solely for the purpose of imparting improved dimensional stability to the sheet. Although other properties of pulp sheets such as tearing strength and folding endurance can be significantly improved by adding long polyester fibres, these same improvements can be effected just as easily and even somewhat better with nylon fibres. This is shown in Table 16 for three webs of the same substance.

As in the case of acrylics and polyamides, the use of polyester fibre alone or in conjunction with woodpulp leads to a number of very attractive properties that can be achieved only, however, at substantially higher cost of the final product. Hence, the main practical use of polyester fibres in

^{*} See, for example, Traut, G. R., Berry, R. C. and Greenman, M. L., Nat. Dos. Eng., 1962, 55, 12

the formation of webs and sheets in the paper field is for high quality specialities.

Olefin polymers

HIGH PRESSURE (low density) polythene with a melting point around 115° C and a remarkable resistance to all organic solvents at ordinary temperatures proved to be an excellent material for extrusion, blow moulding, injection moulding and vacuum forming, but, owing to its inherent softness and to its greasy touch, it did not offer much promise for the formation of rigid fibrous webs. As soon as (with Ziegler catalysts) low pressure (high density) linear polythene with considerable stiffness and a melting point around 135° C became available and then, through the discoveries of Prof. Natta, isotactic polypropylene with an even higher rigidity and with a melting point around 175° C was developed into a commercial product, successful attempts were made to lay down on a papermachine webs of staple fibres made from these polymers either alone or in conjunction with any of the other thin cut filaments described in the preceding paragraphs.

A particularly strong incentive for such efforts was the fact that by 1965 linear polythene was available in bulk at 15-20 cents/lb (with an average specific gravity of 0.95) and there was good reason to believe that in the not-too-distant future isotactic polypropylene (with a specific gravity of 0.90) would also come down to a price of 25-20 cents/lb.

Fibres of both materials are hydrophobic, do not hydrate or fibrillate and cannot be converted into a self-bonding web on a papermachine. Copolymers of ethylene and/or propylene with polar monomers such as vinylacetate, acrylic acid or maleic anhydride can be made self-bonding, however, either alone or with the homopolymers—if necessary, with the aid of binders and anchoring agents—and can be connected into webs of low specific gravity, which are completely moisture resistant and have interesting properties in tensile, tearing and bursting strengths.

Prolonged experimentation with hydrocarbon polymers and fundamental studies of their intrinsic properties did, however, create doubts whether the standard papermachine with water as a carrier would really be the best method to produce fibrous webs of polyolefin filaments and whether there could not be developed a dry casting process that would completely eliminate any liquid carrier and thus provide a simpler and cheaper method to arrive at paper-like structures from synthetic fibres.

Fibrids

SINCE about 1910, the spinning of thin and uniform fibres from polymer solutions has developed into an increasingly refined science and technology.

Around 1930, the corresponding technique of melt spinning was worked out for polyamides, polyesters and polyolefins. During the same period, there grew the know-how of producing thin, transparent and homogeneous films from polymer solutions and polymer melts.

During all these years, it could not fail to happen that sometimes filaments assumed a ribbon-like shape and films displayed a tendency to fibrillate. Accidental observations of this kind and inventive imagination for the creation of new compositions of matter eventually led to production from a liquid polymeric system through an orifice (round, star-shaped or flat) of a continuous strand of finely subdivided matter that occupies a position between a fibre and a film and might be a preferred object for the production of two-dimensional webs either on a papermachine with water as a carrier or, in a further step of simplification, without any carrier in a dry web-casting operation directly from the delivering orifices.

Numerous attempts have been made along these lines by many organisations, but it seems that the most elaborate disclosure of the existence and preparation of such systems is contained in several du Pont patents [such as U.S.P. 2 999 788 (1961), U.S.P. 3 081 579 (1963) and U.S.P. 3 117 053 (1964)] in which for entities intermediate between a fibre, a network and a film the word *fibrid* was coined. It is easy to define a fibre numerically by its average length and cross-section and, equally, to characterise a film by its width and average thickness, but it is rather difficult to give a quantitative geometric description of a certain type of fibrid.

Fibrids are being defined as plexifilamentary strands of interconnected assemblies of fibre and film-like entities, partially embedded in a very thin ribbon-like matrix, also as slashed tubular filamentous systems ranging from fine fibrous networks to very thin ribbon-like assemblies. Characteristic for all of them is a very large specific surface (up to $50 \text{ m}^2/\text{g}$) and a pronounced capacity to form web and sheet-like structures either alone or as binders for other conventional web-forming fibres. The water-binding capacity, adhesivity and softening of fibrids can be varied over a very wide range, since it has been possible by adequate methods to prepare such a system from virtually all synthetic polymers ranging from rigid, high melting polyamides and polyesters to soft and rubbery polyurethanes and polyethers.

There are many ways of preparing fibrids or fibrid-like systems from many synthetic polymers.

One of them is to form a very thin polymeric fibre (less than 0.02 mil) by an interphase polymerisation process, withdraw the film in the form of thin collapsed tubes, orient the macromolecules of the tubes by stretching, then shred the resulting system to an irregular mass of coherent fine filaments, which form an infinite network of fibrous and ribbon-like entities. This

Polymer web formation

method has been successfully applied to prepare fibrids of virtually all polymers that can be synthesised by the interphase polymerisation technique. When suspended in water at a concentration around 0.1 per cent and deposited on a screen to form a waterleaf hand-made sheet or processed on a standard papermachine, these fibrids are capable of forming webs alone, but they can also act very effectively as binders for other filamentous web forms. In the preceding paragraph, an acrylic fibrid 101 and a polyamide fibrid 201 have already been mentioned.

According to the nature of the fibrid-forming polymer and of the properties of the resulting materials, the inventors have distinguished between 'hard' and 'soft' fibrids. Hard fibrids are made, for example, from 66 nylon, 610 nylon, from polyesters such as polyethylene terephthalate, polyurethanes such as the polymer of 2,5-dimethylpiperazine and the *bis*chloroformate of hydroquinone or polyureids such as the reaction product of 2,5-dimethylpiperazine and an aromatic di-isocyanate.

All products present white, fluffy fibrous systems with high melting points (above 180°C and up to 300°C), complete insensitivity to water or organic solvents, large specific surface areas (above $2 \text{ m}^2/\text{g}$ and up to $5 \text{ m}^2/\text{g}$ as measured by the BET method) and, as a consequence, a considerable water-binding capacity (more than 10 g water per 1 g of fibrid), partly by adsorption of water at polar sites on the surface of the fibrids, partly by capillary condensation. Expressing the water-binding capacity in terms of the drainage of a dilute aqueous suspension of the fibrids, one has found that their Canadian standard freeness ranges 150–500.

Sheets made of these materials by hand or on a papermachine are superior to all fibre-based sheets in tensile, tearing and bursting strengths, in elongation, abrasion resistance and in a favourable ratio of wet strength to dry strength.

Another method of preparing fibrids is by adding a solution of a polymer to a precipitating liquid under conditions of very rapid precipitation and very high shear. Almost any polymer (or copolymer) can be used, so long as its molecular weight is high enough (above 20 000, preferably in the range $50\ 000-150\ 000$) and solutions of moderate concentrations are poured into the precipitant under vigorous stirring in the form of a very thin stream. The resulting translucent web-like structures are then disintegrated mechanically. Hard fibrids have been made by this method from polyacrylonitrile, from copolymers of acrylonitrile with minor quantities of such comonomers as vinylacetate, methacrylate, methylmethacrylate or vinylpyrrolidone; from copolyamides consisting of 6, 66 and 610 nylon and from copolyesters containing terephthalic acid and isophthalic or *p*-hydroxybenzoic acid as components. These fibrids also present white, fluffy masses with melting points

5—с.р.w. і

up to 250° C, specific surface areas up to $60 \text{ m}^2/\text{g}$ and water absorbencies up to 15 g water per 1 g of polymer. These can be readily formed into webs by hand or on a papermachine and furnish sheets with superior mechanical, thermal and chemical properties.

Soft fibrids are preferably made by the precipitation method and can be obtained from a wide variety of soft and elastomeric polymers. One group is represented by *block* copolymers of polyester or polyether segments linked together by aromatic di-isocyanate stretches. Segmented linear condensation polymers of this type are well known in the technology of elastomeric fibres (Spandex fibres); they can be readily converted into fibridic structures, if moderately concentrated solutions of them are poured as a fine stream into a precipitant, then broken up by vigorous agitation. Another group of soft fibrids is made from elastomeric addition polymers such as plasticised PVC or PMMA and copolymers of butadiene with acrylonitrile or styrene. Fibrids of this type are white, fluffy, low melting and organic soluble systems that have specific surface areas and water-binding capacities similar to those of the hard fibrids and form webs that excel through their elongation, elasticity and recovery power even from considerable strains.

Interesting compositions have been made by using hard and soft fibrids together in many variations of materials and proportions. Random webs of representatives of the two families can be laid down on a papermachine from conventional stock densities, with a high drainage on the wet end of the machine and with special plastic bonding capacity in the press and dryer section. Sheet construction and properties cover a very wide range from relatively thick, soft, felt-like embossed and needled non-woven fabric to very sheer lace-like and knitted-like tissues having exceptional tensile, tearing and bursting strengths in the dry and wet states.

Another equally attractive use of hard and soft fibrids of all kinds consists of the construction of layered structures, which consist of alternate webs made from hard and soft fibrids and laminated to each other either by pressure alone on the basis of their intrinsic adhesiveness or with the aid of small quantities of suitable adhesives. If one laminates on a hard fibrid web (polyamide, polyester, acrylic or vinyl polymer based) of about 1 mm thickness a soft fibrid web (vinyl, acrylic or polyurethane based) of the same thickness, then on top of it again a hard fibrid web of any appropriate thickness and composition, one obtains flexible, tough and abrasion resistant sheets of controllable porosity for air and moisture vapour, but much superior to natural leather in their softness and dimensional stability when immersed in liquid water for even prolonged periods and at elevated temperatures. These leather-like, layered structures can be passed through a pair of rolls—one hot and the other cold—whereupon one side of the sheet assumes a smooth soft and dense character just like the skin side of finished leather, the other side becomes fibrous, rough and porous, strongly resembling the flesh side of a finished sheet of leather.

Compositions of this general character have been made in a variety of thickness, colours (from snow white to jet black), porosities, unit weights and filler content; all of them are very uniform, can be cut, sewn or glued and represent a new, interesting synthetic sheet material for many applications. Corfam sheets are examples of a certain family of fibrid-based, layered structures.

Hard fibrids can be made not only from wholly synthetic polymers, but also from cellulosics (U.S.P. 3 114 747), preferably from alkaline cellulose xanthate solutions. If a viscose containing 5 per cent cellulose, 9 per cent sodium hydroxide and 26 per cent carbon disulphide is coagulated by a 20 per cent ammonium sulphate solution in a blender at about 10 000 rev/min and the xanthate is regenerated to cellulose by 2.5 per cent sulphuric acid at somewhat elevated temperature while the high shear is maintained, one arrives after washing at a white, fluffy fibrid-like mass. Systems of this type can be cut to staples of different length, oriented by stretching, blended with other fibres, binders and anchoring agents to form fibrous regenerated cellulose webs having a wide variety of properties and potential applications.

The intense and prolonged occupation with fibrid-like systems, which represent a spectrum of intermediates between uniform fibres and homogeneous fibres, has led to still another method for their production, based on the very rapid spinning of a polymer solution or melt in the presence of a blowing agent. It was known to produce thin paper-like sheets from foamed thermoplastics such as polystyrene, polyvinylalcohol, PVC, polythene and polypropylene and their existence led to additional inventive steps for producing fibrid structures instead of homogeneous fibres. If one takes a 7 per cent solution of linear polythene with a melt index of about 0.5 (see particularly U.S.P. 3 081 519 (1963) to du Pont) in methylene chloride at 210°C (corresponding to a pressure of about 650 lb/in²) and extrudes it at high speed (5 000 m/min or more) through a system of spinneret holes, one obtains plexifilamentous strands with total deniers of 200-500, consisting of an interconnected network of fibre-film entities, the diameters of which range 1-50 microns. These fibrid-like strands have tensile strengths of 2-4 g/den, a modulus of 2-15 g/den and an elongation to break between 50 and 100 per cent; they can be highly oriented by drawing and assume tensile strengths up to 16 g/den, moduli up to 240 g/den and still show an elongation to break of around 8 per cent. It is probable that these exceptional properties are the consequence of an unusually high degree of orientation of the macromolecules in the very fine filaments and in the very thin films of the slashed initial tubular structures. Several hydrocarbon polymers such as polythene.

polystyrene, polypropylene, copolymers of them and polyblends have been successfully used to prepare fibridic strands in this property range.

All types of such olefin polymer strands can be dispersed in water either alone or in combination with other fibres or fibrids and, if necessary, in the presence of suspending agents and webs of them can be formed on a papermachine. The existence of dry, fluffy, strong and tough strands and fibrids of this type, however, stimulated additional inventive activities that ultimately led to techniques for producing fibrous webs of considerable width, remarkable homogeneity and outstanding mechanical, thermal and chemical properties *without any liquid carrier*, directly through the formation of highly crimped filaments and fibridic strands and their deposition by mechanical or electrostatic means (see U.S.P. 2 117 055 (1964) to du Pont), using the random character of the original elements and their web-forming, self-bonding character at elevated temperatures or in the presence of appropriate bonding agents.

Some of these spun, bonded webs have already found interesting application in the non-woven fabric field (Reemay of du Pont), others are now developed into thin opaque, printable sheets of high tensile, tearing and bursting strengths and of complete insensitivity to moisture and most chemical agents. If sheets of this type are based on inexpensive polymers such as polythene, polypropylene or PVC and if the basic principles of their webforming character are fully understood, these materials will present an entirely new and very interesting material for packaging, printing, photography and as tape for recorders, computers and other modern communication devices.