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SYNTHETIC PAPERS

UNCONVENTIONAL PROCESSES AND PROPERTIES RELATED TO SPECIAL END USES - A CONCENTRATED REVIEW

B. G. RÅNBY, Department of Polymer Technology, Royal Institute of Technology, Stockholm, Sweden

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Introduction

PAPER-LIKE products or paper substitutes made largely from synthetic polymers are classified as *synthetic paper*, as recently proposed from Japan.[1] Several different types have been developed and the most important are in the following three groups—

1. Spunbonded sheets.
2. Paper-like polymer films (including foamed sheets).
3. Synthetic pulp products.

In addition, there are various combinations of synthetic polymers with pulp fibres that have been developed, tested and used as paper products—for example, addition of synthetic fibres to pulp fibres, impregnation of pulp fibres with synthetic polymers, lamination of paper and board with synthetic polymers and graft copolymerisation of synthetic polymers to pulp fibres. Some of these processes and products are well known and conventional (such as lamination) and some are experimental only (such as grafting)—they will therefore not be further described here. One type of synthetic pulp called *fibrids* was developed early as a thermoplastic binder in paper.[2, 3] In principle, fibrid technology is related to synthetic pulp production (group 3).

There are several reviews and books published on synthetic papers—for example, Battista,[4] Wolpert,[5] Johnson,[6] Lunk & Strange,[7] Inagaki,[8] Kossoff[9] and others.[10, 11]

Spunbonding

THIS technology has been developed in U.S.A. originally by Du Pont (1965) and later by other companies.[12] A dissolved or melted polymer at elevated

Under the chairmanship of Prof. V. T. Stannett temperature and pressure is extruded into a medium, which precipitates or solidifies the polymer into fibres that form a coherent fibrous mat or sheet. The products are calendered, dried, stretched and sometimes coated. It gives a very tough paper-like or non-woven sheet material. Its most striking property is its extraordinary tearing strength, but also its tensile strength, wear resistance and dimensional stability can be developed remarkably. The spunbonded sheets are unusually resistant to water, chemical and biological degradation, so they are used for many special purposes. A large volume is used as base material for carpets, but fibre reinforcement in laminates of various types are also important end uses. Spunbonded sheets of HD polythene (Tyvek), polypropylene (Typar), polyamides (such as Nomex) and polyesters (Reemay) are produced commercially by Du Pont in a wide variety from thick non-transparent mats to the finest open scrims.

Paper-like polymer films

SYNTHETIC paper made from polymer films (usually pigmented), coated in various ways have been developed during the last 4–5 years, mainly in Japan,[13] but also elsewhere.[14] The products have high tensile strength, they are not affected by water and they give an extraordinarily fine surface for colour prints, maps, tracings, etc. They can be made very thin and soft and still retain acceptable opacity for two-sided printing. These synthetic papers were widely advertised a couple of years ago and held as potential large volume products. These prognoses have materialised only to a limited extent. Film-based synthetic papers are to be considered as special products, which eventually will find applications in which their special properties can justify their use. The development of the technology is to a large extent related to the pigmenting and coating problems. The paper-like films may also be foamed to give added bulk, opacity and printability.[15] Foaming can also give added stiffness to a polymer film.

Synthetic pulp products

A THIRD and more recent development are the synthetic paper pulps that have been foreseen for some time, but only in the last few years brought into commercial operation using adequate processes.

Papermaking from synthetic fibres was known on pilot-plant scale even in the fifties.[16] The products have properties related to those of non-woven fabrics and they have been used for very special applications, when the high cost of the paper material could be accepted. Synthetic fibre papers are made from staple fibres of proper dimensions, suspended in water, usually containing a binder system, then formed into sheets. Fibrillating fibres may not need a binder.[17] Paper products from Vinylon (polyvinyl alcohol), nylon, rayon, polyacrylonitrile and polyester fibres have been developed and produced for the limited markets available. The relationships between the constituent fibre properties and the resulting papers have been studied.[18]

Recent developments have given a new type of potentially very inexpensive synthetic pulp fibre materials. According to the information available, these pulps are produced either from the reaction product directly after the polymerisation or made from granulated resin. At this time, technical material has been released about synthetic paper pulps from polythene developed and produced by Crown Zellerbach Corpn. in co-operation with Mitsui Petrochemical Co. and from polypropylene, developed by Ube-Nitto Kasei Co. Ltd., Japan. These new synthetic pulps will be described more in detail.

The Crown Zellerbach/Mitsui product has the trade name 'synthetic woodpulp' (SWP).[19] The SWP is a water-dispersable thermoplastic fibre product containing largely HD polythene and made by a direct method—that is, directly from the reaction mixture after polymerisation. The SWP fibres are of dimensions, that can be made similar to softwood pulp (for example, 75 per cent retained on 20 mesh screen), similar to hardwood pulp (70 per cent on 35+65 mesh screens) and similar to groundwood pulp (50 per cent through 150 mesh screen). The SWP fibres have an average length of 1–4 mm and average coarseness of 3–10 decigrex. Conventional woodpulp fibres have an average length from 0·5 mm (groundwood) to 5 mm (softwood) with an average coarseness of 10–20 decigrex. The semi-commercial grades of SWP show good stability as slurries in water, probably due to their high zeta-potential (−36 mV). The individual SWP fibres have about the same tensile strength as conventional woodpulp fibres, but the elongation to break is several times higher.

The outstanding property of SWP fibres is their easy wettability and dispersability in water (that is, their hydrophilic nature). They require no specific mechanical treatment during papermaking and they blend well with conventional papermaking pulps. The SWP slurries have a high drainage rate with a freeness of 700° CSF, with only very little tendency to flocculate. They do not require refining to develop paper strength. The SWP sheets give opacities of 90–95 per cent with a sheet strength of 0·4–0·06 kg/15 mm (60 g/m^2 sheet). The thermal behaviour of SWP papers are related to the thermoplastic softening and melting of the fibres. Sheets of pure SWP begin to shrink at temperatures of about 120° C and melt at 130°–135° C. Mixed with a conventional woodpulp at a 50:50 ratio, however, the sheets do not shrink even at 145° C. The optical properties of 100 per cent SWP sheets are 95 per cent brightness (Elrepho), 96–97 per cent TAPPI opacity and scattering coefficient of 1 200–1 300. The tensile strength of a sheet to which increasing amounts of SWP fibres are added decreases considerably because of the decreased internal bonding. The tear resistance increases when 20 per cent SWP is added and decreases with additional amounts. The dimensional stability of a sheet increases with increasing amounts of SWP. The wet tensile strength of an SWP sheet increases with heating up to 135°-143° C, when it reaches 90–100 per cent of the dry tensile strength.

Synthetic pulps from polythene, also reported to be made by a 'direct' method, are produced on pilot-plant scale by Solvay & Cie (Belgium) in co-operation with Chubu Chemical Co. (Japan).

The recommended applications for SWP mixed with various amounts of conventional woodpulps are lightweight papers with high opacity and good printing surface, water resistant papers and film-like sheets, which are heat-treated to obtain thermoplastic bonding. Other recommended applications are bonding agents for non-wovens (for example, from rayon fibres) and as laminates that can be embossed. Mixing SWP with a conventional pulp gives lightweight sheets (0·3–0·4 g/ml) of high porosity and high water absorption of the sheets when soaked in water.

Synthetic pulps from polypropylene have been marketed by Ube-Nitto Kasei Co. (Japan) under the trade name DanPulp.[20] They have in many respects properties similar to those of SWP, but of course a higher softening temperature. The DanPulp samples are produced from split yarn and have fibre dimensions similar to conventional woodpulps; they are soft, water dispersible and lighter than SWP pulps. They easily absorb oils and have good chemical resistance. When blended with conventional papermaking pulps, they give sheets that can be thermo-processed. When converted in conventional paper processes, DanPulp pulps can be recovered from waste paper materials. The outstanding properties of both SWP and DanPulp are versatility both in blends and as pure stock. In recovery, they are superior to film-based and foamed synthetic paper. In the paper industry, the synthetic pulps can be introduced without considerable changes in technology. So far as it can be judged now, the combination of low price, interesting properties and versatility make synthetic pulps a promising new variety of papermaking materials.

Several other companies have reported developments of synthetic papermaking pulps from polythene and polypropylene (Chisso Corp./Tukushu Paper Co., Hitachi Chemical Co./Jujo Paper Co., Showa Denko Co., Sumitomo Chemical Co. and Mitsubishi Rayon Co.), from polyacrylonitrile (Mitsubishi Chemical Co. and Toray Industries Co./Kanzaki Paper Co.) and from polyolefin/polyvinylalcohol mixtures (Nihon Synthetic Co.).

The most recent developments in the field of synthetic paper have been presented at an IUPAC-EUCEPA symposium in June 1972[21] and independently reviewed by Hentschel.[22]

Discussion of synthetic papers versus wood-based papers

DURING the last few decades, the commercial possibilities and prospects of synthetic in competition with wood-based paper materials have been discussed repeatedly. Generally, the raw material situation and the general economy have been considered to favour the wood-based papers in the long perspective. The forests are a renewable resource, when properly managed, whereas synthetic paper production is based on fossil fuels as raw material. There are now, however, new aspects brought up in this discuussion, due to changing conditions in world economy and in industry. The wood-based pulp and paper industry is found to be a very serious source of pollution for water and air and therefore detrimental to the human environment. Furthermore, the production of wood-based paper materials with present technology requires very large amounts of external energy, of which the main part is supplied by burning fossil fuel. This external energy is used in the forests for planting trees, fertilising, logging, hauling, barking and chipping the logs; in the pulp and paper mills, for pulping, bleaching, beating and drying pulp sheets and paper products. Adding all energy requirements together, it is probable that the production of 1 kg of paper material consumes larger amounts of non-renewable fossil fuels than the same weight of synthetic polymer products. The pulp and paper industry thus contributes to the energy crisis. In addition, energy production has serious environmental effects. Synthetic polymer production, on the other hand, does not consume more than totally about 5 per cent of the petroleum and natural gas supply, whereas burning for heat and power consumes 85–90 per cent. Increasing prices for fossil fuels and a foreseen shortage of petroleum and gas may affect the burning of these resources rather than restrict their use as a chemical raw material. As a conclusion, the industrial and commercial prospects for synthetic paper products are more favourable than previously anticipated. Synthetic woodpulps may well be a successful large product in the foreseeable future as a complement to wood-based papermaking pulps.

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Transcription of Discussion

Discussion

Dr K. Ebeling I would like to draw attention to two points—stress relaxation and change of modulus. I used dry paper in my study of moisture content (determined by Karl Fischer titration below 0·25 per cent). I did not observe the Kubát behaviour; there was no clear break point when plotting the relaxation speed against the unrelaxed load. The behaviour that I observed was similar to that in your Fig. 9 for the 4 per cent curve.

The other point is that the apparent initial straining modulus decreased after cycling that involved apparent plastic deformation. Only during cycling with relatively high average load did one observe that the slope of the load elongation curve was higher than the initial slope starting from zero load.

Mr A. A. Robertson We clearly have differences between us to resolve. We, too, have carried out these tests under completely dry conditions (at least as dry as anhydrous calcium sulphate can provide) and obtained the Kubát curves for a wide variety of papers. We have been able to relate the local modulus (which we measure after stress relaxation) to a local cycling modulus that also has been determined. We have found the local cycling modulus anywhere along the stress/strain curve to be higher than the initial modulus and very close numerically to that measured after stress relaxation. So our results are in direct contrast to your own.

Dr A. de Ruvo I think that Dr Robertson touched upon very important matters—what is the mechanical effectiveness of the latex in the paper structure and how do different ways of polymer deposition in the paper influence the mechanical effectiveness of the polymer? In our studies, we have worked with a torsional pendulum to measure the amount of polymer that is effective by following the damping curve with temperature. At the glass temperature, the polymer displays a damping peak, which is proportional to the amount of polymer present and mechanically active in the system. Of course, there are different ways in which the polymer can be deposited in the paper. One way is that it is between the fibres, where it constitutes the fibre bond; this is the

Under the chairmanship of Prof. V. T. Stannett most effective way if you want to use the polymer properties. The other way is on a free segment, where it is not taking any mechanical action at all; this is a very poor way of using the polymer. For Fig. G, where we have plotted the area of damping against the amount of binder, we used two different ways of putting the polymer into the system—spray bonding and beater addition. The curve shows that spray bonding is much more effective as indicated by the much higher increase in the area of the damping peak at specific loading levels.

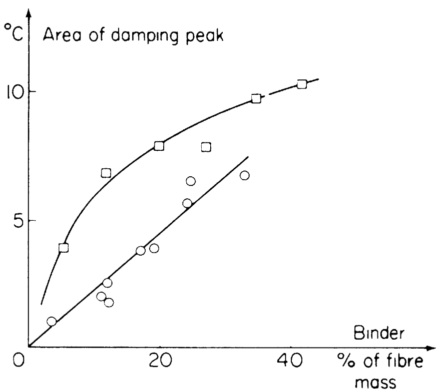

Fig. G

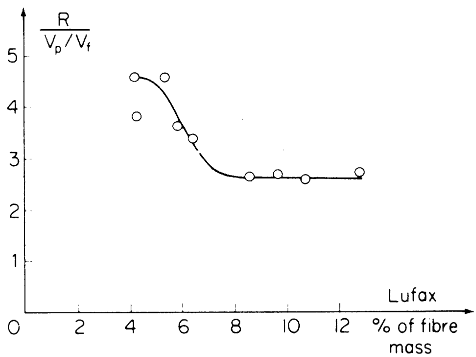

Fig. H

The same situation is shown for a more practical property—strain. Spray bonding is again the effective process for putting the polymers into the sheet.

A small comment about the colloidal system. Of course, when you are using better deposition, you have to have a colloidal system and use a retention agent. In Fig. H, we have plotted binder retention against the percentage of the retention agent (Lufax, in this case). As expected, if we overdose the system, the binder retention falls. What is important is that, exactly at the point where the retention falls, the mechanical effectiveness (that is, the damping area) also falls. This means that the mechanical effectiveness of the latex is reduced by changes in the colloidal system. Besides this, of course, the reduction of retention means that an excess of latex exists in the papermachine system, which can be rather difficult.

Discussion

Mr L. M. Lyne With the increasing limitation of petroleum in the world, do you see a limitation in the development of polymer papers over the next 25 years?

Prof. B. G. Rånby No, I don't see that, because it is a very small fraction of the petroleum that goes into the preparation of polymers. It is at present only about 5 per cent, but the burning of petroleum is 85–90 per cent, so it is in this that restrictions in petroleum usage must first apply.