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NEW POLYMERS[1]

by

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During the last few years, the list of newer polymers commercialised around the world has grown substantially. Many of these are exotic, high priced speciality plastics that will have little or no commercial application for developing countries for some time to come. Others, however, are aimed at many of the same markets where the "commodity" plastics such as polyethylene, PVC or polystyrene are now being used. In some cases, the new polymers are intended to improve upon rather than replace these materials (e.g. as an impact modifier); in others they are substitutes and finally in some markets they are attempting to create new applications where existing polymers could not meet property requirements. Similarly, the newer fibres appear to be both replacements and extenders of existing synthetic fibres.

The developing countries must keep abreast of these developments for several reasons, the most important of which initially is their use in fabricating finished products for export and possibly local use. Local polymer production may not be feasible for some years, but the plastic fabrication industry is likely to compete against plastic products made from these new materials both at home and abroad.

The following table and discussion describes a brief background on each polymer, producers, applications and most recent pricing.

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United Nations Industrial Development Organization

Interregional Petrochemical Symposium on the Development of the Petrochemical Industries in Developing Countries

Baku, USSR, 20 - 31 October 1969

SUMMARY

NEW POLYMERS[1/]

by

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It is important that developing countries keep up to date in developments in new polymers as these products will be more and more used for fabricating finished products or they may also compete with the more conventional plastics production of which has already been established in the developing country concerned.

A list of the new polymers is then given showing the major producers and their current status as a commercial venture and, in some cases, the raw material required.

Poly 4-methylpentene 1 (TPX) is interesting in view of its lightness and transparency, polybutene 1 (isotatic) is still at the development stage but shows promise in regard to its environmental stress cracking

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and temperature resistance.

Ionomers are co-polymers of ethylene with acrylic acids neutralised with cations. They are of considerable value in packaging in view of their oil resistance.

Chlorinated polyethylene has particular good weathering resistance, it can be used to modify the impact properties of PVC and might logically replace the latter.

Saturated polyesters, which are thermoplastics, produce mouldings with excellent engineering properties and will compete with nylon, polyacetyl and even some thermosets.

Nylon 9 is of interest due to the possibility of its synthesis from soyabean oil.

Trogamid T which is a transparent polymer made by condensing trihexamethylenediamine with terephthalic acid is an expensive plastic with valuable engineering properties.

Phenylene oxide polymers have outstanding heat resistance and, blended with polystyrene, are becoming a commercial proposition.

Polysulphones have some useful electrical properties.

Polyimides and their derivatives are another group of temperature resistant products with, in addition, excellent electrical properties. Their high price limit their use to speciality application.

In the next section of the paper some new developments in synthetic fibres are mentioned.

A US silk like fibre "Qiana" is believed to be a polymer obtained by the condensation of dodecane dicarboxylic acid and bis(4-aminocyclohexyl) methane. It has already made good progress in fashion fabrics.

Poly paraethoxybenzoate has been developed in Japan as a silk like fibre. Semi-commercial production of Isotactic and syndiotactic PVC fibres are reported while a wool-like fibre based on a vinylchloride - vinyl alcohol co-polymer has been produced in Japan.

Water soluble polymers are next briefly considered and a short section is devoted to thermoplastic elastomers.

Polypeptides, photopolymers and radiation polymerization make up the final paragraphs of the paper.

Selected Producers of New Polymers

A. Plastics

1. Commodity and Engineering Plastics	Selected Producers	Status	R.M.
4-methylpentene-1	ICI (UK)	Commercial	Propylene
Polybutene-1	Mobil (US)	Semi-	
	Huels (FRG)	Commercial	Butene-1
Ionomers	Du Pont (US)	Commercial	Ethylene
Chlorinated Polyethylene	Hoechst (FRG)	Commercial	
	Dow (US)	Commercial	Ethylene-
	ICI (UK)	Semi-commercial	Chlorine
	Showa Denko (Japan)	Commercial	
Injection Mouldable Polyesters	AKV (Holland)	Commercial	
	Glanzstoff (FRG)	Commercial	
	Teijin (Japan)	Commercial	
	Hoechst (FRG)	Semi-commercial	
Nylon 9	U.S. Department of Agriculture	Development	
	Huels (FRG)	Commercial	
	Emser (Switzerland)	Commercial	
Nylon 12	Dr. Plate (FRG)	Commercial	
	Toyo Rayon (Japan)	Commercial	
Trogamid T	Dynamit Nobel (FRG)	Commercial	
Polypeptides	Several	Semi-commercial	
2. High Temperature			
PPO, Noryl	GE (US)	Commercial	
Polysulfone	Union Carbide (US)		
	Du Pont (US)		
	Monsanto (US)		

Polyimides	American Cyanamid (US) Rhone Poulenc (France)	
Polyamide-Imides	Amoco (US) Westinghouse (US)	
3. Water Soluble		
Polyethylene Oxide	Union Carbide	Commercial
Polyacrylamides	Several	Commercial
Polyethylenimine	BASF (FRG) Dow (US) Chemirad (US)	Commercial Commercial Commercial
4. Thermoplastic Elastomers	Shell	Commercial
B. Fibres		
Qiana	Du Pont (US)	
Polyesterether	Polyester-ether Fibre Dev.Co. (Japan)	Commercial
Polyvinyl alcohol/PVC	Kokoku Rayon and Pulp	
Casein-acrylonitrile	Toyo Rayon	
Polylactones	Kanegafuchi	
PVC (including syndio-tactic)	Rhone Poulenc (France) Montecatini (Italy)	
C. Photopolymers		
5. Printing Plates	W.R. Grace (US) Du Pont (US) Time (US) Union Carbide (US) FMC (US) Bayer (FRG) BASF (FRG) Showa Denko (Japan)	Semi-commercial Semi-commercial Semi-commercial Semi-commercial Semi-commercial Semi-commercial Semi-commercial Semi-commercial

Poly 4-methyl-pentene-1

In 1965 ICI introduced "TPX" 4-methyl-pentene-1 polymers. The monomer for these stereoregular polyolefins is made by polymerization of propylene. TPX provides an interesting balance of properties - low density (0.83) transparency, good temperature resistance, and electrical properties. The material is high priced ($.90-1.25/lb.), has relatively poor load bearing properties and UV resistance, exhibits softness and high water and gas permeability. Its properties have directed uses for injection moulded transparent labware, food housings, medical components, electrical components, automotive light housing - several packaging applications are under development as are copolymers which offer improved properties. Labware, medical (e.g. syringes) and automotive applications (e.g. light housings) appear to offer the greatest opportunity. The high cost and selected property disadvantages may limit TPX to speciality applications rather than as a replacement for the large volume, commodity plastics such as polypropylene.

Polybutene-1

Isotactic polybutene-1 (called polybutylene in some countries) is a semi-commercial olefin polymer with promising properties indicating use in pipe, film, wire coating, adhesives, injection and blow moulding, blending, colouring and other applications. Commercialization has been slowed by processing problems related to this polymer's unusual crystalline phase; the need for copolymers in certain applications and relatively high raw material and polymerization costs relative to other olefin derived polymers. The advantages of polybutene-1 includes excellent environmental stress crack and cold flow resistance, high temperature capabilities, and good burst and tear strength. In the United States polybutene-1 pipe has been used for several engineered pipe applications (e.g. water distribution) and is under evaluation for others (hot water pipe in particular). In Europe, large diameter polybutene-1 water and industrial pipe are under evaluation. Film applications under study include fertilizer bags, consumer produce bags and shrink film (meat). Copolymers for coating of certain wires (run at slower speeds) has been under development; high molecular weight polybutene-1 may compete against the polyisobutylene for hot melt adhesives; it is being blended with HDPE and polypropylene to enhance impact strength and processability. Colour compounding is another potential outlet as higher filler loadings reduced mixing time and good wetting properties have been noted. Injection and blow moulding will probably be limited to large items such as milk crates. Prices in the U.S. currently are in the $0.30-0.40/lb. range and might be as low as $0.20 in the future depending on several factors such as plant size, raw material cost.

Ionomers

The polymers were introduced in 1965 by Du Pont ("SURLYN"). They are essentially copolymers of ethylene with methacrylic or acrylic acid partly neutralized with cations such as sodium and zinc. They offer a number of property improvements over polyethylene, particularly in packaging, notably superior to oil barrier, clarity and puncture resistance. For industrial mouldings, excellent impact strength is a major attribute. Packaging applications probably accounted for well over 50% of 1968 consumption (e.g. extrusion coating of paper and foils, skin and blister packaging) but use for blow moulded containers, injection moulded components, footwear (boxtoes, top lifts, soles), foam (insulation), adhesives, portend expanded use. Prices in 1968 were in the 40-50cts./lb. range but could decline below 40cts./lb. as volume increases.

Chlorinated polyethylene (CPE)

Although not "new" (Hoechst in Germany has offered PVC/CPE compounds for many years) CPE has gained increasing acceptance in the U.S. and more recently in Japan as an impact modifier for PVC. CPE is produced by gas phase or slurry chlorination of HDPE (LDPE is used by one firm). The type and molecular weight distribution of the PE chlorine content, distribution, crystallinity etc. influence final properties. A large number of grades can be produced by controlling these variables. Most commercial CPE polymers are based on 30-40% chlorination. Prices in the U.S. are 30-35 cts./lb. Modification of rigid PVC for outdoor building products (e.g. pipe, sheet, floor tile, windows, rainwear, etc.) looms as the most important application area. CPE provides much improved weathering characteristics over competitive modifiers, while enhancing impact and processing. Calendered film and sheet may be a major outlet as flexible procucts with minor amounts of plasticizer have been made - replacement of PVC would be the logical replacement. In Japan, Shouw enko has developed ACS, (the C segment is ?? and replaces the butadiene or B portion of ABS) which reportedly exhibits better weathering and flame resistance.

Injection Mouldable Polyesters

Technical improvements in Europe and Japan have led to processable thermoplastic polyesters that have excellent strength, hardness, wear resistance, low moisture absorption, good electrical and temperature properties. These materials are expected to compete with other engineered plastics such as nylon and polyacetal and some thermosets. Elimination of previous processing problems has been achieved by the combined addition of nucleating agents - glass fibre, increasing molecular weight and developing special moulding conditions. The presence of inexpensive polyester raw materials for fibres in many countries raises the attractiveness of reduced prices for the thermoplastic polyesters (30 glass filled types are priced at about $0.60-$0.70cts./lb. in Japan). In Japan, thermosets as well as engineering thermoplastics are the subject of polyester market development, particularly for electrical automotive and other industrial components. In Europe, applications include mechanical products (e.g. gears); hardware (e.g. handles); chemical (e.g. valves); appliance houses and electrical items.

Nylon 12

This butadiene based polymer exhibits the lowest density melting point and water absorption of the available polyamides. Its price/property balance points to competition with nylons 11 and 610 (both of which are derived from price sensitive natural castor oil). However, it is not likely to replace either in all applications since its price is still high and what appears to be minor property differences actually make replacement very difficult. Production is presently in Europe and Japan. Major uses will include automotive and industrial tubing; packaging film; moulded products requiring good dimensional stability; high performance wire coatings; monofilament and fluidized bed coatings. Relatively little replacement of the cheaper commodity nylons (6, 6/6) is expected, thus limiting nylon 12 to a high priced speciality material. A key determinant in future pricing may be the success of new butadiene based fibres which utilize the same intermediates required for synthesis of nylon 12. Their success might lower material costs considerably. To date, nylon 12 has been most successful in replacing nylon 11 in Europe. Its success against nylon 610 (and 11) in the United States has been negligible. Japanese promotional efforts are underway.

Nylon 9

The U.S. Department of Agriculture has synthesized nylon 9 from soybean oil as a potential low cost material with properties akin to those of the other low density, low moisture nylons. Development is continuing with economic utilization of byproducts still a problem. In the USSR nylon 9 (fibre) reportedly has been produced by telomerization of ethylene. Japanese scientists have synthesized nylon 9 by ozolysis of sperm oil.

Trogamid T

This European produced polyamide is transparent and has good surface hardness, shrinkage and low creep, compared to engineering plastics such as polycarbonate, polyacetal and nylon 6. It is a condensation product of TMD (trihexamethylenediamine) and terephthalic acid, priced at about $1.70/lb. Future prices will depend mainly on the cost structure of the TMD which is expensive. Volume was less than 0.5 million pounds in 1968. Polycarbonates, metals and to a smaller extent other nylons will be the replacement target of Trogamid T. Applications already commercialized include transparent housings, electrical and industrial components.

Phenylene Oxide Polymers

Phenylene oxide polymers were commercialized by General Electric in 1964 and trademarked "PPO". They were highly publicized because of their high temperature properties and novel polymerization technique - oxidative coupling - utilized in their synthesis. The subsequent discovery that high concentrations of polystyrene (e.g. 50%) could be blended with PPO led to an expansion of the original "family". These polystyrene modified resins trademarked "Noryl" sacrifice some of the high performance properties of PPO but their lower cost flame retardance and good all-round mechanical properties result in a favourable price/property balance and have gained strong acceptance in many applications previously specifying acetal, nylon, polycarbonate and ABS etc. Currently PPO (itself modified with polystyrene) remains a high priced ($1.00/lb.) resin used mainly in selected high temperature electrical/electronic, water, military and medical applications; in contrast Noryl is specified for a number of radio and television components; many business machine housings; appliance parts; water components, (e.g. pumps, sprinkler) and various electrical/electronic components. Noryl (unfilled) is priced from $.059 - $0.75/lb. and new grades are expected to be priced lower mainly to compete with high heat ABS and related "commodity" polymers. By the mid 1970's consumption of modified phenylene oxide polymers could pass 15,000-20,000 tons in the United States alone. The further development of oxidative coupling portends further breakthroughs in polymer synthesis.

Polysulfone

Union Carbide introduced this high temperature material in 1965 (it is based on bisphenol A and dichlorodiphenylsulfone). Applications have been concentrated in the electrical/electronics field (e.g. connectors) and plated appliance components, automotive and aircraft parts, as well as several specialized products. High price ($1.00/lb.) and failure to penetrate wire coating have limited initial sales to less than 2,000 tons in 1968. Replacement of thermosets (e.g. special purpose phenols, DAP) in electrical products such as circuit breakers may expand production in the future.

Polyimides, Polyamide-imides, Polyester-imides

Usage of these high temperature polymers has been concentrated in electrical, aerospace and military markets where performance rather than price dictates material specification. All three materials are used as for wire and cable varnishes and enamels; polyimides are predominate for high temperature film, moulded components, adhesives and reinforced plastic binders. The polyimides are the reaction products of dianhydrides such as pyromellitic dianhydride (PMDA) and 3, 3', 4, 4' - benzophenone tetracarboxylic acid dianhydride (BTDA), and diamines such as m-phenylene diamine or methylene dianiline. The amide-imides are based on trimellitic anhydride (TMA) and certain diamines; the polyester-imides are produced by reacting TMA or other anhydrides with aromatic diamines and polyalcohols. Wire enamel and varnishes will continue to be the largest outlet followed by insulation film; usage for adhesives and reinforced plastic binders in supersonic aircraft is expected to increase substantially. Proprietary high cost equipment is required for fabrication of film, moulded parts and several other items. Sales volume will be low but dollar value will be high. Polyimide fibres are under development.

Fibres

Qiana

Du Pont announced this new "silk-like" fibre in 1968. Initial use was in women's high fashion fabrics, but future sales are expected to include a much wider segment of the consumer apparel field and eventually industrial fabrics. The first samples of Qiana indicated silk-like properties plus good colour, clarity, dimensional stability, drape, wrinkle, pleat and crease resistance and ease of care. Introductory prices were $5-8/lb. Qiana is probably derived from dodecanedioc acid and the diamine bis (4-aminocyclohexyl) methane (PACM). The acid is synthesized from butadiene and the diamine from aniline and formaldehyde. Some forecasts indicated a volume of 100-200 million pounds by the late 1970's. Other silk-like fibres have been synthesized in Japan as noted below.

Polyester-ether

Three Japanese companies - Mitsubishi Chemical Industries, Kokoku Rayon and Pulp Co. and Daiwa Spinning Co. formed the Polyester-ether Development Company to promote their joint efforts on a silk-like fibre "A-Tell". Starting from phenol, the synthesis yields the linear polymer poly (paraethoxybenzoate) or PEB. Reportedly, the fibre has better alkali resistance than polyester fibres, excellent weather resistance, good elasticity, high shrinkage and is readily dyeable. Prices were about $4.50/lb. in 1968. Suggested applications include clothing, household fabrics and industrial items.

Lactone Based Fibres

Fibres based on polypiralactone have been produced in semi-commercial quantities in Japan and the United States. Other potential end uses include film and sheet, medical sutures and moulded products. One Japanese firm indicates that these fibres may be competitive with spandex. Several lactones have been under study - piralolactone appears to be favoured because of its superior hydrolysis resistance.

PVC

PVC homopolymer and copolymer fibres have been produced for limited usage where their chemical resistance, flame retardance, low melting point collectively were desirable. More recently firms in Italy, France and other countries have developed syndiotactic PVC polymers which reportedly can be used as high as 130°C without shrinkage, thereby enhancing washing in hot water and exposure to most dry cleaning solvents. Continued interest in flame-retardant fibres is likely to increase PVC based fibre blends. Low temperature polymerization is a key aspect in the synthesis of these syndiotactic polymers.

PVC/Polyvinyl Alcohol

A vinyl chloride/polyvinyl alcohol graft copolymer has been developed by Toyo Chemical Company in Japan. Called "Cordela", the fibre reportedly has wool-like properties. Several guides have been announced, including a type which is self-extinguishing, easily dyeable, and has good stability and abrasion resistance. Fabrics where flame retardance is needed will be a major objective of this fibre.

Water Soluble Polymers

Polyethylene-oxide, polyacrylamides, and polyethylenimines are not new, but they have all undergone renewed growth in recent years due to expansion of old markets and development of new ones. High molecular weight polyethylene oxide is used for sizing of glass fibre and other textiles; friction reduction and coagulation (mining, petroleum), industrial and agricultural film and several speciality uses, including pharmaceuticals. Prices are $0.60-$1.50/lb. in the United States; polyacrylamides are the largest volume material of the three (U.S. consumption about 10,000 MT in 1968); they are used as coagulants in water treatment; mining; as dry strength resins and retention aids by the paper industry; for friction reduction by petroleum producers. Acrylamides are also used in a number of water insoluble applications. Polyethylenimines have found widening use as a paper industry drainage age, flocculent, adhesive and for various textile uses. Collectively more than 30,000 tons of these polymers will be used for water soluble applications in the United States by 1974.

Thermoplastic Elastomers

Styrene-butadiene-styrene block copolymers commercialized by Shell Chemical offer the properties of elastomers and processability of thermoplastics. Other firms (e.g. Phillips Petroleum) have developed competitive products. While volume is still relatively small, rapid growth is expected during the next decade. With only slight adjustments, conventional injections moulding machinery can be used for the SBS polymers. Most of the 1968 production was diverted to shoe soling applications, sponge soling and processing aids; in future years other growing outlets will include coatings, adhesives, hot melts, pharmaceuticals, various extruded products, toys, wire and cable.

Polypeptides

Several advances have benn made in polypeptide derived polymers. Production of proteins from petroleum has received considerable publicity. Less has been said on polypeptide fibres, films and synthetic leather. In Japan, polyglutamic acid and polyalaline fibres are under development. These silk-like materials are readily dyeable. U.S. research groups have produced films from polypeptides with good mechanical and temperature properties. Several Japanese firms are now manufacturing synthetic leather based on poly (R-methyl-L-glutamate) which is used for shoes, interior home furnishings, etc. This relatively new product is expected to achieve further commercial success in other countries.

Photopolymers

Photopolymers are used in the production of printed circuits, integrated circuits, industrial etching, and more recently for plastic based printing plates. The latter application is intensive effort in many countries for newspaper printing (photoengraving or photolithography). A diverse number of substrates and photopolymer systems have been presented to the printing industry for evaluation. Polymers used include nylon, polyester, acrylic, polyacetal, polyethylene oxide-phenolic, DAP and others. The plastic plate is intended to eliminate some of the steps currently required in newspaper printing.

Radiation

Radiation polymerization is gradually becoming commercially feasible for an expanded number of products. Already it is used for curing of paints and certain fabricated plastics; graft polymerization for textile fibres; crosslinking of polyethylene foam, film and other substrates; wood/polymer building items; production of "hard-to-make" copolymers, polymer degradation, and more recently polymerization of polyethylene and polyacetals (semi-commercial).

14 . 1 . 72