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Reviews

Polymers for Extreme Service Conditions

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ABSTRACT: The article reviews briefly the presently existing organic polymers which have particularly high rigidity, tensile strength, thermostability, and resistance against chemical deterioration. They are used in the form of fibers, films, and composite systems whenever light weight is essential in combination with the above-mentioned mechanical, thermal, and chemical properties. Significant progress has been made in the last decade through the synthesis of new materials such as linear polyaromatic polymers and networks therefrom in combination with new methods of transformation and application.

(I) Introduction

Polymeric materials for extreme and unusual service conditions represent one of the stimulating moving fronts of macromolecular science and engineering. Usually such materials have been made to satisfy certain existing extravagant demands of rather limited scale but in many cases any improvement in the availability of raw materials in the case of their processing characteristics or in their properties could open important and, sometimes, even large new fields of application. As a consequence they should well be considered as attractive targets for attractive research and development efforts.[1] Since demands and performance depend to a large extent on the mode and character of application it would appear appropriate to present, in this brief report, the existing information according to such special groups as fibers, films, membranes, adhesives, and composites.

In each class: (1) the essential critical properties will be enumerated, (2) the presently used materials will be described, (3) the existing methods for their application will be discussed. Whenever possible indications will be given for improved materials and processes in the future.

(II) Fibers

Although most materials discussed here are made of organic polymers it will be useful to include a few other fibrous systems for comparison. There are several properties which characterize "extreme" performance; some of the most important of them are: high rigidity (modulus in tension or Young's modulus), high tensile strength, high resistance against elevated temperatures and radiation, high resistance against swelling, dissolution, and chemical deterioration.

Young's modulus is determined by nondestructive tests such as differential reversible extension or the propagation velocity of sonic waves; it is a quantity referring to two equilibrium states (the undeformed and the strained) and can be calculated or, at least, estimated from information on the atomic or molecular structure of the sample and from the forces which hold these elementary particles together. The data required have been accumulated over the last 50 years with increasing dependability and accuracy with the aid of most modern physical methods: scattering and absorption of x rays, electrons, light, IR and microwaves, NMR, thermal and chemical measurements, and others. One basic quantity is the *binding energy* between adjacent atoms or molecules; the presently accepted ranges are given in Table I[2] in electron volts. To convert these figures approximately into kilocalories one has to multiply by 23.

In order to go from the binding *energy* to the binding *forces* one needs the total potential energy as a *function* of distance. Such functions have been developed over the years in literature with improving accuracy; Figure 1 shows the general character for van der Waals, ionic, covalent, and metallic binding. Significant for the calculation of the *forces* is the *derivative* of the *energy* curve such as shown in Figure 2. The slope of the derivative at the point U_0 of the *energy curve* is the *modulus* in tension (Young's modulus) and the steepest slope of the energy curve right of U_0 gives the breaking or *tensile strength*. These values can be determined and represent the theoretical modulus and theoretical breaking strength of the material under consideration. Table II contains data on Young's modulus of a variety of filamentous materials in psi and dyn/cm^2. The conversion factors are:

$$1\ \mathrm{kP/cm^2} = 14.3\ \mathrm{psi} = 10^6\ \mathrm{dyn/cm^2}$$

High-modulus, high-strength fibers have considerable practical importance as *reinforcing* agents in flexible, elastomeric systems, such as radial tires, transport belts, and vehicle tracks, but also as *stiffening* elements in rigid thermoplastics and thermosettings such as propeller and compressor blades, wingtips, and others.

The *first* application needs for satisfactory performance moduli are in the range of 5–20 million psi (0.35–1.4×10^6 kP/cm^2) and tensile strengths from 0.5 to 0.7 million psi (35 000 to 50 000 kP/cm^2). Extreme cases of use are the

Table I[a]

Bonding type	Binding energy, eV
van der Waals (without permanent dipole moment)	~0.1
van der Waals (with permanent dipole moment or hydrogen bonding)	0.3–0.5
Covalent	2.0–10
Metallic (no partially filled d shells)	1–5
Metallic (transition metals with partially filled d shells)	4–10
Ionic (monovalent ions, such as alkali halides)	5–8
Ionic (multivalent ions, such as alkaline earth oxides)	10–18

[a] For specific examples: the energy of the O–H bond in water is 5 eV and that for the single C–C bond in organic molecules is 2.5 eV.

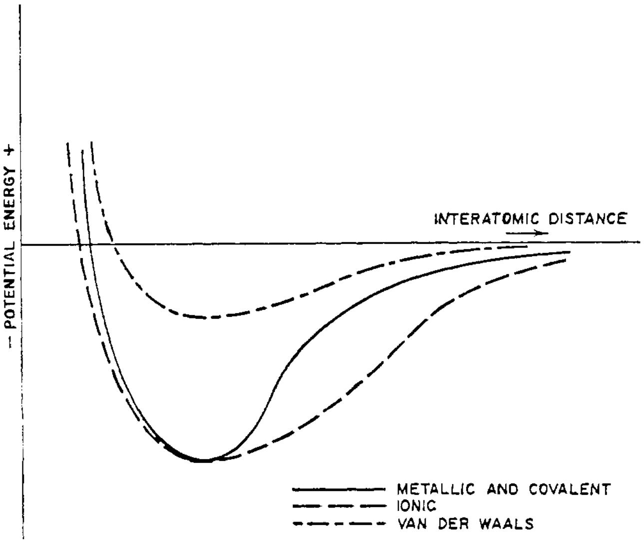

Figure 1.

Table II
Moduli of Highly Oriented Organic Fibers in Comparison with Other Rigid Materials

Material	Tensile modulus dyn/cm² × 10⁻¹¹	psi × 10⁻⁶
Polyethylene	3–7	4.5–10
Polypropylene	1.6	2.2
Polyoxymethylene	2.3	3.2
Poly(vinyl alcohol)	4.0	8.4
Cellulose	2.5–3.0	3.5–4.5
Poly(para aromatics)	8–10	11–14
E glass	7.3	10.2
S glass	8.7	12.2
Steel wire	Up to 20	28
Graphite fiber	Up to 80	110

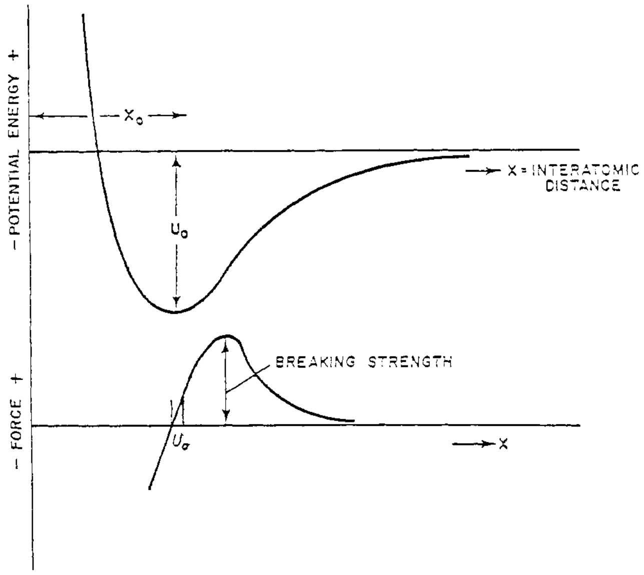

Figure 2.

landing tires for the Concorde, the 747's, DC 10's, and all supersonic military aircraft and also for the tires of heavy earth moving equipment and heavy agricultural vehicles and for the elastomeric parts of fast moving transport belts in heavy chemical industry and in the construction of superior battle tanks. In all these uses the filaments must also be *tough;* i.e., their elongation to break should not be less than 5% so that they can endure many million cycles of bending, they must adhere firmly to the elastomeric matrix, they must be resistant against chemical attack, and they should have a low specific gravity.

Three materials are presently available for extreme service conditions in this field: steel wires having a special surface treatment, glass fibers with a particularly high elongation to break, and *Kevlar,* an aromatic polyamide developed by du Pont which bonds particularly strongly to rubber and has the lowest specific gravity (1.3 against 2.5 and 7.5). It is probably fair to expect that each of these materials will occupy that part of the critical condition domain for which it is best suited or adjustable and it is also probable that the youngest competitor, Kevlar, will still undergo substantial improvements by product and process changes such as a modified chemical composition, higher molecular weight, different spinning technique, and more sophisticated aftertreatments.

Much has been said in the past on the great impact which, in the late 1920's, the classical work of Carothers[3] and his associates on adiphatic polyesters and polyamides had on the entire field of man-made fibers and it is highly cited as an impressive example for the indispensible value of fundamental research on the developments of new techniques. A step of similar importance was achieved by Morgan and his associates[4] some 30 years later by the discovery of the *low-temperature* synthesis of *aromatic* polyesters, polyamides, and other polyaromatic systems which cannot be prepared by the classical, thermal process and have already provided for a surprising number of rigid, strong, and thermally stable fibers which consistently proved to survive extreme service conditions, where all older materials have hopelessly failed.

Frequently, in the past, the availability of a novel technique to prepare a family of new substances has led to additional discoveries. This was also happening here because it was found that several of the stiff chains, particularly the aromatic polyamides, aromides, display a surprising tendency to aggregate in solution and in the melt and have been used to obtain filaments of exceptional rigidity and strength which are opening quite new and unexpected areas of application.

The *second* extreme service condition for fibers is their use as reinforcing elements in hard and strong resins, thermoplastic and thermosetting, for the construction of parts in spacecraft, airplanes, cars, boats, buildings, and in many fast running machines from ventilator fans to textile spindles. The classical case for the overwhelming success of this approach is the complete conquest of small boat construction, with sails or motors, by glass fiber reinforced unsaturated polyesters. The critical properties for these severe service conditions are: highest possible modulus and strength, perfect bonding with

Table III
Representative High-Modulus, High-Strength Thermally Stable Fibers

	Modulus		Tensile strength	
Material	psi × 10^6	kP cm^{-2} × 10^6	psi × 10^3	kP cm^{-2} × 10^3
B_4C	80	5.5	425	30
UTRC glass	20	1.4	770	53
AL_2O_3	50	3.5	350	24
C-PAN	75	5.2	310	21
C-PAN	48	3.3	400	28
C-Rayon	78	5.3	380	26
C-Pitch	37	2.5	500	35
BN	40	2.8	300	20
	Theoretical value in kP cm^{-2} about 5–7		Theoretical value in kP cm^{-2} about 300–500	

Table IV
Companies Engaged in HM-HT Carbon Fibers

Company	Precursor	Density	Modulus, psi × 10^6	Tensile strength, psi × 10^3
Celanese	PAN	1.96	75	310
Polycarbon	PAN	1.71	35	340
Great Lakes	PAN	1.8	48	400
Hercules	PAN	1.8	37	400
Hitco	Rayon	1.72	50	310
Morganite	PAN	1.88	58	360
Stackpole	PAN	1.78	30	480
UCC	PAN	1.77	34	450
UCC	Pitch	1.8	35	500

the matrix, low specific gravity, and easy processibility (all along machinability). Table III contains the best presently available materials for this purpose. B_4C was recently studied[5] and gave excellent results; it is not yet available commercially but might well become a particularly important member of the class of extra performing materials. A great deal of interesting work has recently been carried out with glass fibers;[6] UTRC glass is a representative material which could be available at relatively moderate cost (as compared with the fibers of the other table) and might well occupy an important position for the "not quite" extreme applications. Two Al_2O_3 fibers are being developed, one by du Pont and one by Sumitomo; they are in the state of early development and show very attractive properties.

The largest and most intensely studied group are the C fibers, "carbon" or "graphite" fibers, which are made from several precursors and cover a wide range of useful properties.[7] Table IV lists the most active producers of high-modulus, high-strength carbon fibers; it reveals that, presently, three precursors are used: PAN (polyacrylonitrile) fiber, normal and highly oriented rayon (in most cases highly oriented), and "pitch", a viscous mesophase prepared by prolonged heating of commercial pitches at temperatures above 350 °C.[8] The literature on the preparation and properties of carbon fibers is already rather extensive[9] and, in this review, it should only be pointed out that the ultimate goal is the attainment of a high modulus (above 50 × 10^6 psi) together with a high strength (around 3 × 10^5 psi) and a relatively high elongation to break (around 2%). In Table III there are not only the measured values of the critical quantities but also "theoretical" values which were estimated by procedures as described above.

Since the determination of the modulus is a reversible, nondestructive test one should expect a reasonable agreement between prediction and observation. In fact, this is the case and all measured values fall either in the theoretical range or somewhat below it. Such moderate deviations to lower values obviously mean that the structure assumed for the sample was an oversimplification. Looking now on the tensile strength values, one finds that there is a substantial difference between the actual values and the theoretical prediction. The reason for this discrepancy is clear: the measurement of the tensile strength is a destructive, irreversible test; the filament breaks at a "weak spot" and its overall structure which was used for the calculation has no relation to the weak spots or irregularities of the sample. Only very careful processing and an increase of the elongation to break can reduce the difference between the theoretical and actual breaking strength. In fact, the present experimental efforts in carbon fiber technology aim at the increase of the elongation to break, e.g., to 2.2%

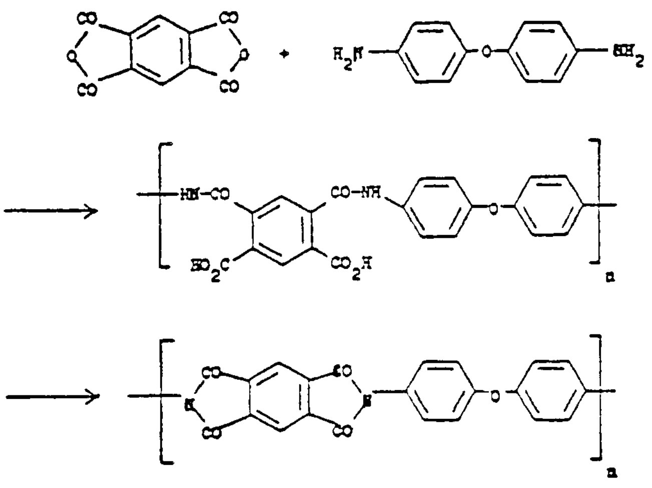

Figure 3. Polyimide such as Kapton.

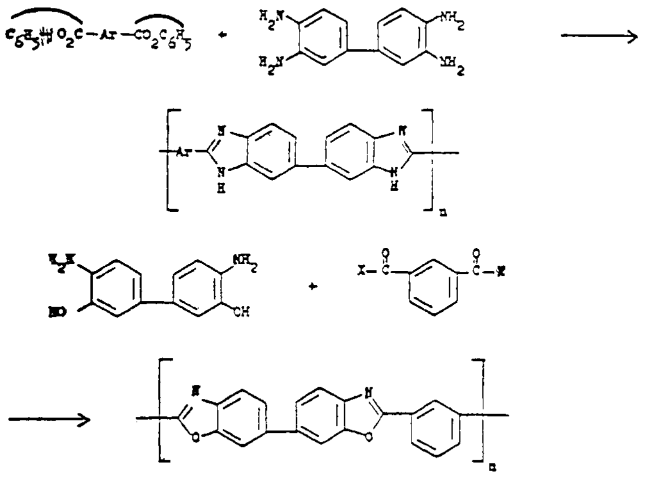

Figure 4. Polybenzimidazole and polybenzoxazole.

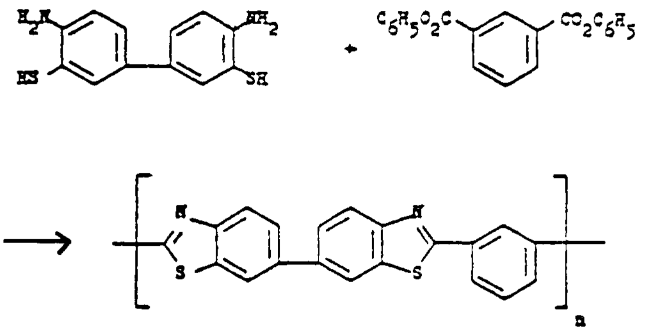

Figure 5. Polybenzothiazole.

from its present value of 1.2%, at a modulus between 40 and 50×10^6 psi because that would probably give a strength between 300 000 and 500 000 psi. No present carbon fiber offers this combination although B_4C apparently does it.

As for resistance against elevated temperatures and chemical attack all materials in Table III with the possible exception of the glass are satisfactory for presently considered applications although the bonding strength and uniformity of C fibers to a resinous matrix such as an epoxy or bismaleimide varies greatly depending on the precursor and on the processing details of a particular fiber. The variety of applications for high-performance fibers is large and attractive; it ranges from golf clubs, tennis rackets and fishing rods over brakelinings, cutting wheels, high-temperature ducts, and exhausts to essential parts of rocket and jet motors, airplane wing tips, and engine nacelles. No wonder that quite a few companies (see Table IV) are now investing considerable efforts to develop the chemistry and technology of such fibers.

There exists still a strong potential for improvement through the use of additional inorganic compounds such as borides, carbides, and nitrides of the lower elements of the periodic table, by other precursors for the preparation of carbon fibers and by improved methods of carbonization and graphitization.

(III) Films and Membranes

In general the use of these two-dimensional systems is very widely spread over such fields as packaging, printing, decorating, and laminating. Practically all existing thermoplastics are used and the techniques of film formation have reached a very high degree of perfection as shown, f.i., by casting speeds of more than 300 yd/min and by the simultaneous blow molding of four and more individual layers from one circular extruder head.

Extreme service conditions are demanded in many different uses and for several different reasons; this report is going to restrict itself to film applications in electronic systems and for solar sailing and also to membrane use in the separation of liquids and the purification of water.

The critical conditions for electronics uses follow: The film should be very *thin* (1 μm or less) without pin holes, very *uniform* (less than 5% fluctuation), a good insulator (resistivity 10^{15} Ω cm or more), resistant to high temperatures (above 200 °C) yet not fragile under cryogenic conditions (down to 2 °K), and should not be deteriorated by moisture, oxygen, and ozone over periods of several years. It would also be desirable to have films with a low dielectric constant (around 2.5) and others characterized by higher values (if possible up to 20).

There are many materials which satisfy most of the above demands in the low-temperature range such as polyethylene, polypropylene, polystyrene, PVC, poly(vinyl fluoride) and poly(vinylidene fluoride), and others. At somewhat elevated temperatures (120–160 °C) polyester (Mylar) normal or biaxially oriented without or with coatings is widely and successfully used. Still higher temperatures require the use of Kel-F, Teflon, aromatic nylons, polyesters, and still more complicated polymers such as polyimides, polybenzimidazoles, polyoxydiazoles, polyquinoxalines, and others.[10] Figures 3 to 8 present the principles of the synthesis and the structural formulas of a few representative materials of this class. Recently wholly aromatic polyesters have been prepared and tested, particularly polymers made from terephthaloyl dichloride and bisphenols such as phenolphthalein, diphenylbisphenol A, and fluorenylbisphenol.

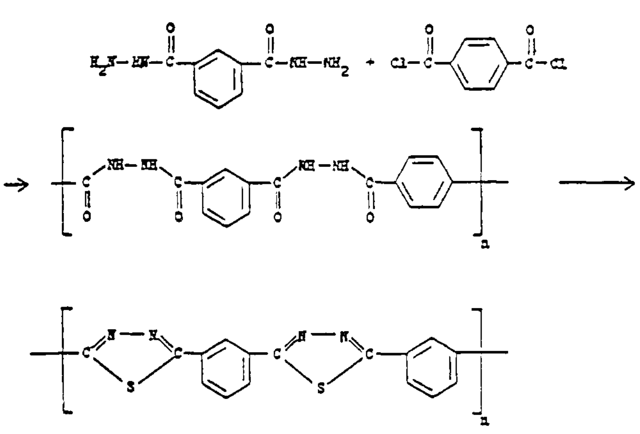

Figure 6. Polyoxydiazole.

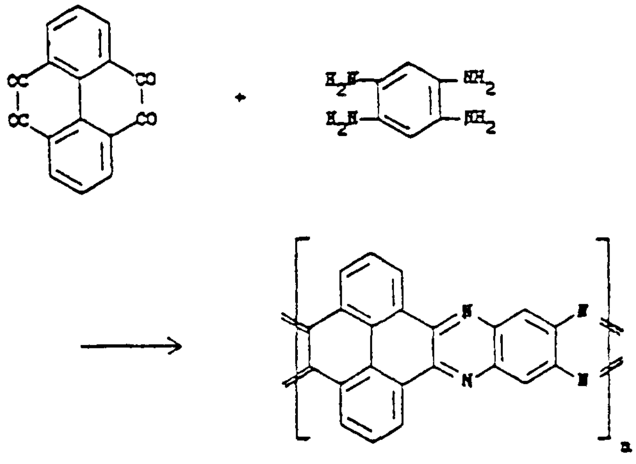

Figure 7. Ladder polyquinoxaline.

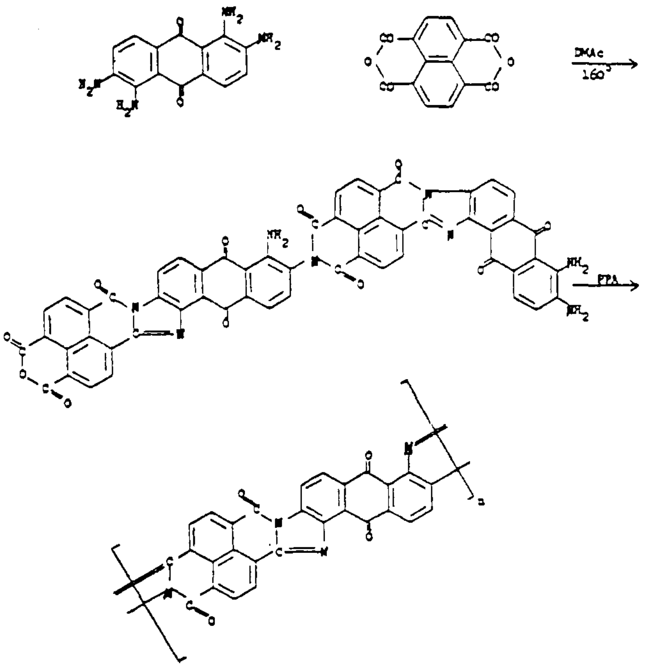

Figure 8. Ladder polypyrrolones.

The attainment of *practically* usable species of all these materials is difficult because of the fact that the melting or softening points of most of these advanced materials are so high that they cannot be cast, extruded, or spun and, at the same time, they are also insoluble or only very difficultly soluble in all available solvents. Several ways are now being tried to overcome this impasse. One way is to prepare a fusible

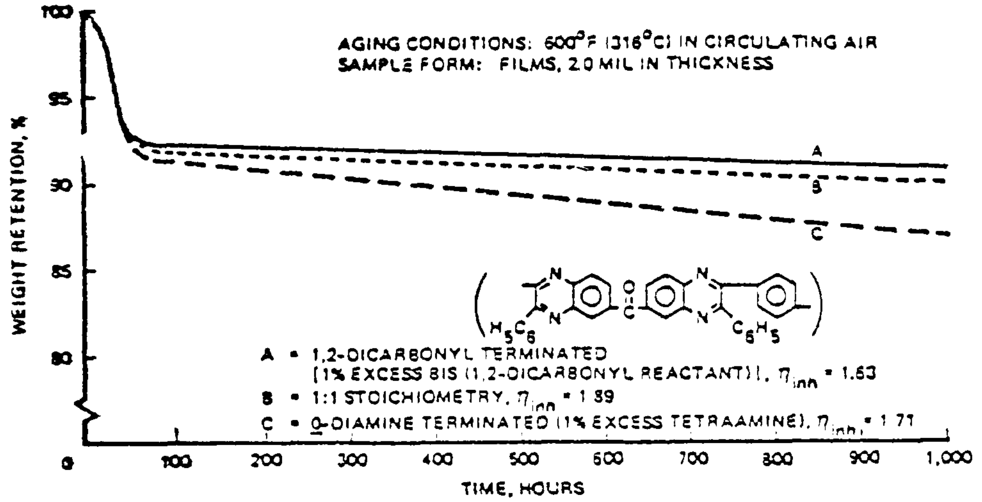

Figure 9. Aging characteristics of a film of poly(phenylquinoxaline) which was cast from solution; see ref 11.

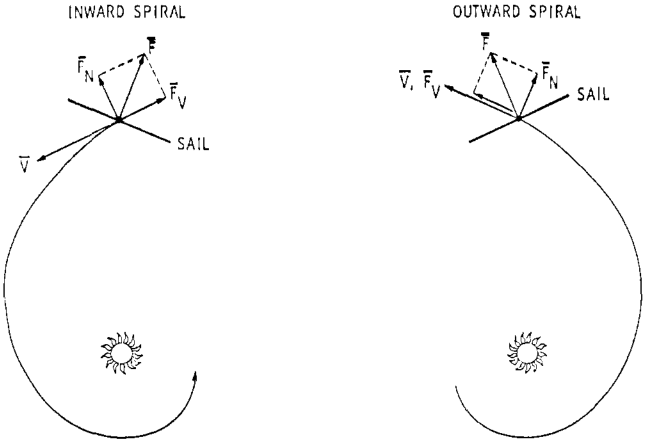

Figure 10. Solar force application.

or soluble *precursor*, cast the film or spin the fiber, and complete the condensation after the form giving step is completed. Polyimide films (Kapton) and fibers are examples for the success of this procedure. Another way is to introduce *solubilizing groups* which do not affect deleteriously the mechanical, thermal, and electrical properties of the material. One such group is the phenyl group which was successfully used to render highly condensed polyheteroaromatics more tractable. Figure 9 shows the aging characteristics of a film cast from a polyquinoxaline which was made soluble by the introduction of phenyl groups in the molecule; after a moderate loss in weight after 50 h the film remains essentially unchanged for 1000 h.[11] In a similar manner, Stille has rendered polyphenylenes soluble by substitution with phenyl groups.[12]

Another large and important use of films or membranes which requires extreme performance is for separation of liquid mixtures and of solvent and solute in solutions. For this purpose a delicate compromise between mechanical and diffusional properties is needed in the interest of prolonged durability under service conditions, f.i., in reverse osmosis. The membrane has to be strong and tough; it also has to permit a reasonably rapid flow through it but, on the other hand, for the purpose of selective permeation it has to be very dense. Presently it is attempted to strike this compromise by preparing systems which have a very dense, thin (down to 0.002 μm) *skin* deposited on a thick (order of magnitude of mils), tough, porous *support*. In fact, this design of a highly *anisotropic* thin membrane, flat or tubular (hollow fiber), on a spongy support has been very successful and has already led to a new and expanding technology for water purification.[13]

The original material applied for this purpose was cellulose acetate which is readily available, relatively easy to cast or spin, and, hence, is still widely used. However, its chemical sensitivity (degradation of the cellulosic chain and hydrolysis of the acetate group) prevents its application in certain cases and limits generally its durability. As a result other polymeric materials are now being tested which would better satisfy the demanding service conditions; they are polysulfones, aromatic polyamides, poly(phenylene oxides), polybenzimidazoles, and derivatives of these classes which provide for the desired degree of solvent permeability. The properties of these highly anisotropic membranes depend on the conditions of their preparation such as concentration of the casting solution, speed of coagulation, nature of the solvent, temperature, and others. It is probable that the use of new materials and improvements in the technique of membrane manufacturing are going to play an important role in water recovery and pollution control.[14]

Still another challenging feature of thin specialty films will be their application in *solar sailing* which is being studied by a research group at the Jet Propulsion Laboratory in Pasadena. Any object in the space of our solar system is exposed to two forces: the gravitational attraction by the sun which tends to pull the object toward the center and the radiation pressure which tends to push it in the opposite direction. Both forces depend on the distance d between sun and object according to

$$F = K/d_2$$

where K is a constant given by the mass and geometry of the object.

If a large, light, and rigid film is placed in space, radiation pressure or gravitation can be made to prevail depending on the position of the plane of the film to the direction of the radiation pressure. Figure 10 shows that the appropriate position of the film may produce motion in any desired direction and, thus, lead to *solar sailing*. Calculations carried out at the Jet Propulsion Laboratory show that a film, weighing 3 g/m^2 (or less) and having an area of 600000 m^2 (or more) would give a solar sail which would be able to carry a substantial payload to any point in the solar system provided that it does not approach the sun too closely. Table V shows a few missions for such transports which would not require the use of any rocket fuel once the object is outside of the gravitational field of the Earth. This obviously leads to the question: can we make such solar sails? They would have to consist of a very light carrier

Table V
Possible Missions for Solar Sail Ships

	Time in years	Payload in kg
Rendez vous with Halleys Comet	4	820
Mars sample return flight	3	4000
Mercury orbitor	1.6	8300
Jupiter: transfer time sail returns to earth	3.3	1800
Saturn: transfer time sail returns to earth	5.5	1600

Table VI
Some Solar Sail Specifications

Carrier	Must not weigh more than 3 g/m^2 Must support 10^9 rods of protons
Film, fabric or web	Must not be affected by UV over 2–3 years Must stand 600 °K over 203 years Must have an emissivity of about 0.20

(film, fabric, or web) which would be coated on one side with a very thin (less than 0.1 micron) highly reflective layer (such as, f.i., aluminum) and on the other side by an equally thin cooling layer (such as, f.i., SiO_2). Table VI contains the (approximate) specifications for the carrier and shows that it should be possible to meet the requirements by very thin films or very fine fibers of several existing thermally stable and radiation resistant polymers. Potential candidates would be, f.i., aromatic polyesters, poly(p-xylylenes) (parylene), together with the materials shown in Figures 3 to 8. The remaining problem from the material side would be to produce them in sufficiently large quantities and to bring them into the form of a very thin film or a very fine fiber. Even though this is a difficult task it is not impossible and, consequently, the Jet Propulsion Laboratory in Pasadena and NASA have initiated projects for a more detailed study of solar sailing. Whatever the ultimate outcome of these investigations will be, it can readily be seen that there will be several interesting "spin offs" for the technologies of thermally stable electronic systems, flame resistant coatings and separator membranes.

(IV) Adhesives

One important factor for extreme adhesive performance is *very rapid setting and binding.* This is not difficult to achieve in melt adhesion, where a viscous layer of the adhesive freezes rapidly upon cooling of the joint. There are, however, cases, in paper and textile industry and particularly in medicine, where the bond formation has to take place at or around room temperature in the shortest possible time. Normally adhesives are polymeric materials dissolved in a liquid which is evaporated to establish the desired joint. This evaporation is much too slow for many purposes and also often causes too much shrinkage during setting.[15] Consequently methods have been developed to effect adhesion by using one or more undiluted polymerizable molecules or compositions which are setting rapidly and completely at room temperature. Several such systems are presently used.

One consists of a mixture of a macromolecular polyether (mol wt between 1500 and 5000) having hydroxyl end groups and a diisocyanate. As soon as this mixture is brought between two pieces of the adherent the components react with each other and with hydroxyl or other polar groups of the adherent and a strong bond results, which, however, needs still a few minutes to be formed. Another similar technique uses a mixture of an epoxy resin (mol wt between 400 and 2000) and a setting catalyst (acid anhydride, polyamine, or boron complex) eventually producing a cross-linked epoxy network which provides for the adhesion. Both methods produce useful bonding with moderate speed but the joints are not resistant against temperatures above 150–180 °C. To achieve bonds with improved thermal stability a new system is presently studied and developed. It uses the reactivity of bis(maleimides) with amines, polyhydroxy compounds, and themselves for the rapid formation of a highly cross-linked aromatic network which possesses polar groups and considerable hydrogen bonding capacity. Maleic anhydride is first reacted with p-phenylenediamine giving a bis(maleimide) with two reactive double bonds. This precursor is fusible and soluble, can be coated onto the adherent, and is polymerized either alone or under addition of more diamine. The bonds are very strong and thermally stable but, for the time being, require for their formation somewhat elevated temperatures and, at least, several minutes.

The fastest adhesion at room temperature without solvent is provided by the almost instantaneous polymerization of α-cyano acrylates. Elaborate studies have established that the setting rate in air depends on the alcohol component of the ester and that the n-butyl and isobutyl acrylate polymerize as a thin layer in the presence of H_2O in less than 1 s and form strong bonds between polar adherents such as paper, fabric, cellophane, and skin.[16]

Another domain which demands extreme service conditions for adhesion is the structural adhesives to be used in the construction of aircraft, vehicles, buildings, furniture, etc. They must combine good surface wetting properties with firm molding to the adherent and with satisfactory aging characteristics over a wide temperature range, i.e., they must remain tough down to temperatures around −50 °C and should not soften or deteriorate at temperatures around 250 °C. Presently the solution of this problem is approached by the use of *curable block copolymers.* The best elastomeric segments of these compositions are silicones and fluoropolymers such as fluorocarbons, fluoroethers, and fluoronitron compounds. Their presence in the molecular weight range between 100 and 1000 is needed to balance the shrinkage of the adhesive layer during curing and to avoid embrittlement through additional cross-linking when the bond has to serve at elevated temperatures over longer periods. These rubbery segments have to be capped or telomerized with multifunctional groups such as the isocyanate, epoxy, nitrile, carbene, or nitrene group which build up the network in the adhesive layer and provide for firm bonding with the adherent either by covalent forces, by hydrogen bonding, or strong polar interaction.

Another (more molecular) approach is now studied through the synthesis and use of special bis(maleiimides). The first step in their preparation is the capping of poly(ethylene oxide) segments (mol wt between 500 and 2000) with amino groups. These liquid intermediates are allowed to react with maleic anhydride to form a liquid or low melting and easily soluble bis(maleimide) which is placed on the surface of the adherent and cures without or with catalysts and additional components through the multifunctionality of the two double bonds of the maleic anhydride. The result is a network of elastomeric ether bonds and of thermally stable cyclic imide units. Adhesives of this type play an important role in the formulation of many composites including those which are supposed to maintain their essential properties under severe conditions.[17]

(V) Composites

The purpose of composites is to attain certain properties or property combinations of polymeric systems which cannot be materialized by the use of a single substance. It is therefore natural to look for composites whenever extreme service conditions are required. This is, in fact, the case whenever

Table VII
AF-R-530/Modmor II Laminate High-Temperature Flexural Performance Retention

Heat Aging	Flexural strength, psi	Modulus, psi × 10^6	% retention of initial strength	Composite wt loss
Room temp	223 200	17.2		
200 h at 600 °F	181 000	16.7	81	1.5
500 h at 600 °F	181 400	18.3	81	3.7
1000 h at 600 °F	86 700	11.7	39	10.7
Room temp	281 500	17.2		
1 h at 700 °F	171 200	18.3		
50 h at 700 °F	172 000	16.9	100	3.1
100 h at 700 °F	143 700	14.5	84	6.5
Room temp	234 300	16.8		
1 h at 800 °F	217 000	16.4	93	0
5 h at 800 °F	143 000	14.8	61	1.5
10 h at 800 °F	48 000	14.2	21	7.5
1 h at 900 °F	171 100	16.0	73	3.0
1 h at 1000 °F	91 100	9.1	39	10

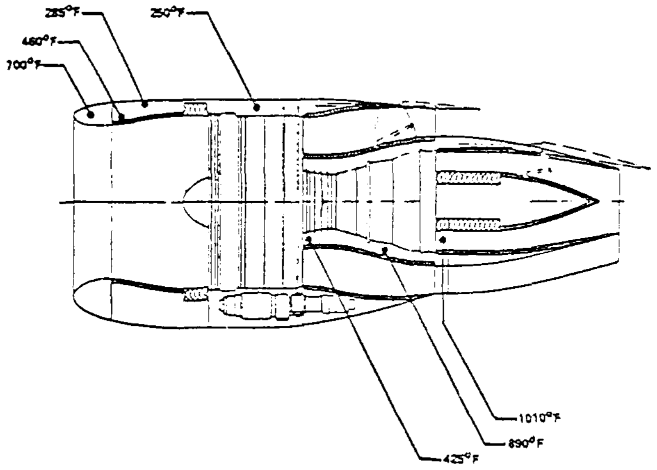

Figure 11. Advanced technology engine.

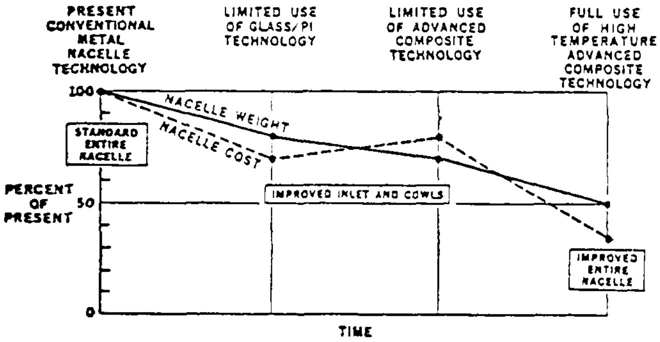

Figure 12. Potential impact of composite nacelle construction.

unusual mechanical and thermal properties have to be combined with exceptional resistance against fatigue, abrasion, and, eventually, chemical attack.

Probably the largest field of composite development and application is the fiber reinforced thermoplastic and, even more, thermosetting resins. For their construction one evidently uses the most advanced fibers, the strongest matrices, and the best bonding agents and combines them as carefully as practically possible. Since the best fibers and adhesives have already been mentioned it may be appropriate to describe in this concluding paragraph a few particularly instructive cases for the use of composite structures which permit progress in areas of extreme service conditions.

Ultralight, very rigid, strong, and nonburning *foams* are being developed by shredding hard foams of polybenzimidazoles, polyimides, and polycyanurates and by molding the pieces into desired shapes with the aid of a bis(maleiimide) adhesive.[18]

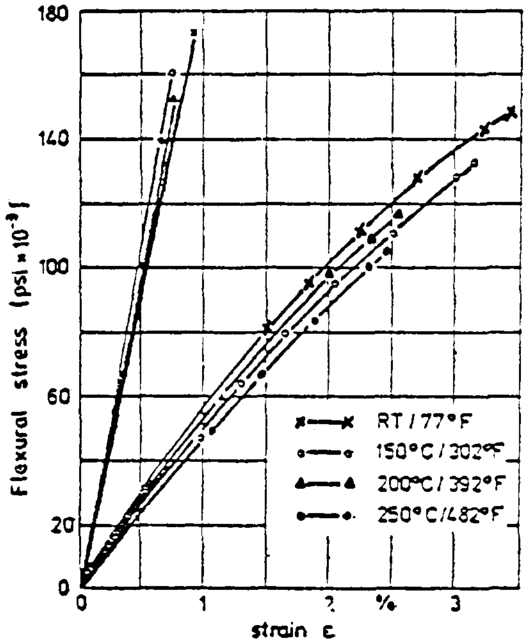

Figure 13. Stress–strain curves of fiber reinforced poly[bis(maleimides)].

A particularly interesting case is the use of nonmetallic composite materials in the design of commercial jet plane engine nacelle.[19] Both acoustical structure, for attenuation of sound in engine inlet and fan exhaust ducts, and nonacoustical structure, for use in other nacelle areas, are under investigation. Unique composite development problems include sustained high-temperature operation and intermittent environmental operating extremes under flight loads, severe sonic fatigue conditions, fire burnthrough resistance, and sound attenuation requirements. A method of composite integral construction shows potential for satisfying many of these extreme requirements. The development and application of a glass fiber/polyimide resin configuration is presented, as well as data on other configurations of interest. A full-scale glass/polyamide inlet acoustical liner for an advanced technology airplane has recently been built and acoustically tested on an engine test stand. Lightweight integral constructions of advanced fibers are in development and undergoing tests. Preliminary analyses show significant cost and weight savings potential. Figure 11 shows the concept of an advanced technology engine. For the areas of highest temperatures (1010, 890, and 700 °F (about 480, 430, and 340 °C)) carbon fiber reinforced polyimide honeycomb or fibercore structures are studied whereas the less heat exposed parts are made from Kevlar or glassfiber filled epoxides. Figure 12 shows the potential impact of composite nacelle technology on weight and price. Corresponding advantages could be reaped if other parts of jet planes, parts of wings and of the cabin, would be manufactured from high-strength, light-weight composites.

Table VI shows the remarkable thermal stability of a carbon fiber (Modmor II) reinforced laminate of a poly(imidazoquinoxaline) (AF-R-530). Carbonization of this material at 1600 °F (800 °C) in N_2 produced structural glassy carbon with char yields up to 85%.[20]

Carbon and glass fibers were used to reinforce unidirectional panels made of bis(maleimides);[23] the composites did not show any loss in flexural behavior even after long exposures to 250 °C. In Figure 13 the straight lines at the left side refer to a loading of 56 vol % with Modmor II fibers, whereas the slightly curved lines at the right side have been obtained with 52 vol % of E glass.[21]

References and Notes

(1) Compare, e.g.: M. A. Golub and J. A. Parker, *Appl. Polym. Symp.*, **No. 22** (1973), or C. Arnold, Jr., "Stability of High Temperature Resistant Polymers", Sandia Laboratories, Sept 1973; International Review of Science, Vol. 8; Macromolecular Science, W. B. Black, "High Modulus Organic Fibers"; also J. Economy, *Appl. Polym. Symp.*, **No. 29,** (1976).

(2) NAS Report on Ultimate Strength of Materials, 1972, also R. A. Swal, "Thermodynamics of Solids", Wiley, New York, N.Y., 1962; "International Critical Tables", Van Nostrand, New York, N.Y., 1963.

(3) Compare, e.g., H. Mark and G. S. Whitby, "Collected Papers of W. H. Carothers on Polymerization", Interscience, New York, N.Y., 1940.

(4) P. W. Morgan, some prominent members of Morgan's "team" are T. I. Blair, S. L. Kwolek, E. Magat, and J. R. Schaefgen.

(5) D. J. Bernsten, W. D. Smith, and J. Economy, *Appl. Polym. Symp.*, **No. 9** 365 (1969).

(6) J. F. Bacon, *Appl. Polym. Symp.*, **No. 29,** 117 (1976).

(7) Compare, e.g.: *Appl. Polym. Symp.*, **No. 9** (1969); **No. 21** (1970); and **No. 29** (1976).

(8) J. B. Barr, S. Chwastiak, R. Didchenko, I. C. Lewis, R. T. Lewis, and L. S. Singer, *Appl. Polym. Symp.*, **No. 29,** 161 (1976), also S. Otani, *Carbon*, **3,** 213 (1965); **4,** 426 (1966).

(9) Compare ref 5 and also H. M. Hawthorne, "Carbon Fibers", Proceeding of the International Conference, London, February 1971; R. Bacon and W. A. Schalamon, "Eighth Biennial Conference on Carbon", Buffalo, N.Y., June 1967.

(10) The literature on high-temperature resistant polymers is very large; here are a few representative references: P. W. Morgan, *Polym. Rev.*, **10,** 1 (1965); D. A. Frey, M. Hasegawa, and C. S. Marvel, *J. Polym. Sci., Part A,* **2,** 2057 (1963); P. E. Cassidy, C. S. Marvel, and S. Ray, *J. Polym. Sci., Part A,* **3,** 153 (1965); J. Preston, and W. B. Black, *J. Polym. Sci., Part B,* **4,** 267 (1966); J. Preston, W. F. DeWinter, and W. B. Black, *J. Polym. Sci., Part A-1,* **7,** 283 (1969); H. Vogel and C. S. Marvel, *J. Polym. Sci.,* **50,** 511 (1961); L. Plummer and C. S. Marvel, *J. Polym. Sci., Part A,* **2,** 2559 (1964); T. V. L. Narayan and C. S. Marvel, *J. Polym. Sci., Part A-1,* **5,** 1113 (1967); V. V. Korshak et al., *Bull. Acad. Sci. USSR, Div. Chem. Sci.,* 1677, 1859 (1963); *Vysokomol. Soedin.,* **6,** 901, 1251, 1394 (1964); *Doki, USSR, Chem. Sect.,* 149, 195 (1963); *Bull. Acad. Sci. USSR, Div. Chem. Sci.,* 743 (1966); N. A. Adrova, M. M. Koton, and et al., *Doki, USSR, Chem. Sci.,* **1,** 166 (1966); V. V. Korshak et al., *Vysokomol. Soedin, A,* **11,** 35 (1969); V. V. Korshak et al., *ibid.,* 11, 22 (1969); C. J. Abshire and C. S. Marvel, *Macromol. Chem.,* 44–46, 388 (1961); V. V. Korshak, E. S. Krongauz, and A. L. Rusanov, *J. Polym. Sci., Part C,* **16,** 2635 (1967); P. M. Hergenrother, W. Wrasidlo, and H. H. Levine, *J. Polym. Sci., Part A-3,* 1665 (1965); Y. Imai, K. Uno, and et al., *Makromol. Chem.,* **85,** 179 (1964); V. S. Yakubovich, N. N. Voznesenskaya, and et al., *Vysokomol. Soedin.,* **9,** 1973 (1967); J. R. Holsten and M. R. Lilyquist, *J. Polym. Sci., Part A-3,* 3905 (1965); A. H. Fraser and W. P. Fitzgerald, Jr., *J. Polym. Sci., Part C,* **19,** 95 (1967); R. L. Van Deusen, *J. Polym. Sci., Part B,* **4,** 211 (1966); A. A. Berlin, B. I. Liogon'kii, G. M. Shamroev, and G. V. Belova, *Izv. Akad. Nauk, SSSR, Ser. Khim.,* **5,** 945 (1966); J. K. Stille and J. R. Williamson, *J. Polym. Sci., Part B,* **2,** 209 (1964); J. K. Stille and E. L. Mainen, *J. Polym. Sci., Part B,* **4,** 39, 665 (1966); *Macromolecules,* 1, 36 (1968); J. K. Stille and M. E. Freeburger *J. Polym. Sci., Part B,* **5,** 989 (1967). More recent publications can be found in ref 1.

(11) P. M. Hergenrother and H. H. Levine, *J. Polym. Sci., Part A-1,* **5,** 1453 (1967); P. M. Hergenrother, *Appl. Polym. Symp.,* **No. 22,** 57 (1973).

(12) J. K. Stille, *Macromol. Rev.,* **5,** 385 (1972).

(13) Compare, f.i., K. S. Spiegler, "Principles of Desalination", Academic Press, New York, N.Y., 1966; also "The Permasep Process" of du Pont, company literature 1970, Wilmington, Del. 19898.

(14) H. K. Lonsdale and H. E. Podall, Ed., "Reverse Osmosis Membrane Research", Plenum Press, New York, N.Y., 1972.

(15) Compare, i.e., J. J. Bikerman, "The Science of Adhesive Joints"; Academic Press, New York, N.Y., 1961; J. A. Clark, *J. Adhes.,* **3,** 295 (1972); R. L. Patrick, Ed., "Treatise on Adhesion and Adhesives", Marcel Dekker, New York, N.Y., 1967.

(16) L. S. Laskin, *High Polym.,* **24,** 105 (1970).

(17) Compare, f.i., S. Mostovoy et al., *J. Appl. Polym. Sci.,* **10,** 1351 (1966); **13,** 1083 (1969), and the Symposium on "Durability of Adhesive Bonded Structures", Oct. 27–29, 1976, to be published as a symposium volume of *J. Appl. Polym. Sci.,* in 1977. Also R. P. Kambour et al., *J. Appl. Polym. Sci.,* **20,** 3275 (1976), and R. P. Kambour, "Block Polymers", Plenum Press, New York, N.Y., 1970, 263.

(18) Compare, e.g., I. O. Salyer et al., *Appl. Polym. Symp.,* **No. 22,** 1 (1973).

(19) Compare, f.i., A. M. Lovelace et al., "Composite Project", Air Force Materials Lab., Dayton, Ohio, August 1972; L. D. Christensen and R. N. Holmes, *Appl. Polym. Symp.,* **No. 22,** 3 (1973).

(20) R. B. Osnel et al., *Appl. Polym. Symp.,* **No. 22,** 21 (1973).

(21) K. E. J. Barrett, *J. Appl. Polym. Sci.,* **11,** 1617 (1970); H. D. Stenzenberger, *Appl. Polym. Symp.,* **No. 22,** 77 (1973).

(22) T. T. Serafini et al., *J. Appl. Polym. Sci.,* **16,** 905 (1972), also T. T. Serafini and P. Delvigo, *Appl. Polym. Symp.,* **no. 22,** 89 (1973).

(23) The bismaleiimides used in these and other studies were prepared by the reaction of an aromatic diamine such as meta- or paraphenylenediamine, benzidine, bisoxyaniline or methylenebis(aniline) with maleic- norbornyldicarbocyclic- and tetrahydrophthalic acid anhydride.[22]