Forschung, Wissenschaft

Requirements of New Polymeric Materials for Heavy Service Conditions

D.W. Van Krevelen **

Arnhem, The Netherlands

Abstract

The concept "property" is discussed in the light of the service conditions of the material. The presently existing polymeric materials are reviewed as regards their rigidity, strength, thermo-stability and resistance against chemical deterioration. Homo-polymers can fulfill the requirements for extreme service conditions only partly, viz in the form of fibers, films and elastomeric tubes, but not as all round engineering materials. For the last mentioned category a special balance of properties is required: light weight in combination with very good mechanical, thermal and environmental properties *in all directions*. Composite systems provide a satisfying solution *provided* that the adhesion between matrix and reinforcement is very good. New methods of fabrication and application will have to be worked out assuring economical use in competition with other engineering materials, e.g. metals and their alloys.

Introduction

The developments of Technology and Engineering—notably in the fields of micro-electronics and space research—need materials to satisfy extravagant demands; this in order to meet extreme and quite unusual service conditions [1].

Requirements on new materials can be expressed in two ways: qualitatively by means of observable trends, quantitatively by means of definable target values of certain properties. In this lecture I shall do both. Before dealing, however, with the requirement of future developments of property combinations, we first of all have to deal with the concept "property" itself.

In my book "Properties of Polymers" [2] I discussed at some length the broad significance of the concept property. This can be clarified if we follow the material on its way, from the unformed material to the final articles made from it.

In the unformed material most of the properties are *intrinsic* or structure-based. In a later stage we become especially interested in the *processing* properties of the material, since they determine its usability and its processing economy. Finally the properties of the material within the end product become the most important because they determine the appearance, the performance and the endurance of the final *article*.

These different classes of properties are interconnected of course. Processing properties are a natural consequence of the interplay of intrinsic properties and processing conditions. Article properties are a consequence of combinations of intrinsic properties and "added" properties, i.e. properties created during processing.

Intrinsic properties

The intrinsic properties are *structure-based*. They can be measured with a high degree of accuracy and reproducibility in the laboratory. Many intrinsic properties can be estimated from *additive molar functions* which are summations of atomic or group contributions per structural unit in the polymer. Table 1 shows a survey of 18 additive functions by means of which 18 different properties of polymers can be estimated from the chemical constitution of the polymeric structural unit.

Some of the intrinsic properties can be combined to dimensionless ratios or *dimensionless material constants*. I mention a few of them.

a. The ratio T_g/T_m, an indicator of the irregularity of structure of the polymeric unit. It goes from 0.4 for the highly regular poly-methylene to about 0.9 for very irregular, more complicated, units. The average value is about ⅔. This dimensionless quantity has a tremendous influence on several phenomena in the polymeric behaviour, e.g. the rate of crystallization of polymers [3] (see Fig. 1). For good engineering materials this ratio must be on the low side.

b. The ratio ϱ_c/ϱ_a, the ratio of the densities of the completely crystalline to the completely amorphous state of the polymer. Its value goes from 1.25 for very regular, simple polymeric units to 1.05 for more irregular units. This ratio is closely related to T_g/T_m; it may be expressed by the formula:

$$\varrho_a/\varrho_c \approx 2/3 + 1/3\, T_g/T_m$$

c. The ratio ν, lateral contraction to axial strain at elongation. It is called *Poisson ratio* and is a measure of the liquidlikeness of a material. Very rigid materials have

* Main Lecture at the 7th International Macromolecular Symposium at Interlaken, May 21–22, 1981.

** Private address: Prof. Dr. D.W. van Krevelen, Bakenbergse Weg 85, 6814 MD Arnhem, The Netherlands.

Table 1:
Additive Molar Functions

TYPE	Additive function	Symbol	Formula	Derived from, and useful for estimation of :
I	Molar weight	M	ΣA	atomic weight (A)
II	Molar volume	V	$M\upsilon = \frac{M}{\rho}$	specific volume (υ) density (ρ)
	Molar heat capacity	C_p	Mc_p	specific heat (c_p).
	Molar entropy of fusion	ΔS_m	$M\Delta s_m$	specific entropy of fusion (Δs_m)
	Molar cohesive energy	E_{coh}	$\Delta H_{vap} - RT = Ve_{coh} = V\delta^2$	cohesive energy density (e_{coh}) solubility parameter (δ)
	Molar magnetic susceptibility	X	$M\chi$	diamagnetic susceptibility (χ)
	Molar free enthalpy of formation	ΔG_f^o	$\Delta(\Delta G_f^o) = RT\ln K_{eq}$	equilibrium constant (K_{eq})
III	Molar refraction	R_{LL}	$\frac{M}{\rho}\cdot\frac{n^2-1}{n^2+2}$	refractive index (n)
	do.	R_{GD}	$\frac{M}{\rho}(n-1)$	do.
	Molar dielectric polarisation	P	$\frac{M}{\rho}\frac{\epsilon-1}{\epsilon+2}$	dielectric constant (ϵ)
	Molar sound velocity function (Rao function)	U	$\frac{M}{\rho}\left(u_{long}\right)^{\frac{1}{3}}\left(\frac{1+\nu}{3(1-\nu)}\right)^{\frac{1}{6}}$	longitudinal sound velocity (u_{long}) Poisson modulus (ν)
IV	Molar thermal expansion	E	$Me = \frac{M}{\rho}\alpha$	thermal expansivity (e) coefficient of thermal expansion (α)
	Molar glass transition function	Yg	MTg	glass transition temperature (Tg)
	Molar melt transition function	Ym	MTm	crystalline melting temperature (T_m)
	Molar attraction function	F	$\left(\frac{M}{\rho}E_{coh}\right)^{\frac{1}{2}} = \frac{M}{\rho}\delta$	solubility parameter (δ)
	Molar parachor	P_S	$\frac{M}{\rho}\gamma^{\frac{1}{4}}$	surface tension (γ)
	Molar intrinsic viscosity function	K	$MK_\Theta^{\frac{1}{2}} = M\left(\frac{[\eta]_\Theta}{\bar{M}^{\frac{1}{2}}}\right)^{\frac{1}{2}}$	intrinsic viscosity ($[\eta]$) average molecular weight ($\bar{M}$)
	Molar refractive index (Vogel function)	R_V	Mn	refractive index (n)
	Molar viscosity-temperature function	H_η	$ME_\eta^{\frac{1}{3}}(\infty)$	activation energy of viscous flow at high temp. ($E_\eta(\infty)$)
	Molar char formation tendency function	CFT	$M\frac{CR}{1200}$	char residu (CR in wt-percentage) on pyrolysis

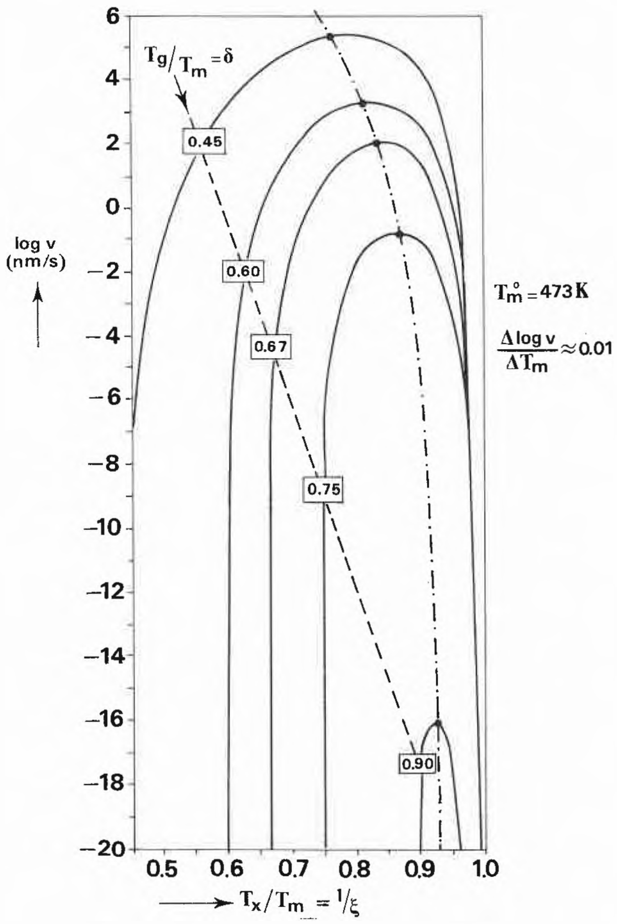


Fig. 1: Master Graph for the growth rate of spherulitic polymeric crystals
(v = linear growth rate; T_x = crystallisation temperature)

values of 0.15, whereas rubbers approach 0.5, the value of liquids. The Poisson ratio is also an indicator to estimate the maximum elongation (to failure) of the material (see Fig. 13.20 in [2]).

d. The *dielectric constant* ε, which goes from 2 to > 10 for polymers. It is also a global indicator of the electrical resistivity of the material (see Fig. 11.4 in [2]).

e. M_w/M_n., the *ratio weight average to number average molecular weight* (= Q). This is an indicator of the molecular weight distribution. It has a very large influence on the viscous behaviour of the polymeric melt at high shear stress and shear rate [4]. Its value goes from 1 for polymers with an ideally uniform molecular distribution (difficult to process) to values of about 30 for polymers with a very wide spread in MW-distribution (also difficult to process in the melt). In the practice of processing, values between 2 and 5 are appreciated.

Processing Properties

Sometimes it is possible to formulate the processing properties in the form of dimensionless groups, in which on the one side the relevant intrinsic properties and on the other side characteristic dimensions and times of the apparatus are represented. Empirical relationships between dimensionless groups have a much wider validity than those between single physical properties. Some examples:

The combination

$$\left(\frac{\varrho \cdot \Delta H}{\lambda \eta}\right)\left(\frac{\Delta p \cdot d^2}{\Delta T}\right)$$

gives a good indication of the processability of a polymer melt in an extruder*).

Another important dimensionless group is the following:

$$\left(\frac{\gamma \cos \theta}{\eta}\right) \cdot \left(\frac{t}{L}\right)$$

which is an indicator of local wetting of a surface by a melt during impregnation*).

If a deeper insight in the phenomena is lacking, one is forced to use purely empirical diagrams with a very restricted validity. Examples are moulding area and mouldability diagrams of one defined polymer on one defined moulding machine (see [5] and [2]).

Article properties

This category of properties is the most difficult for objective evaluation since in most cases the physical back-

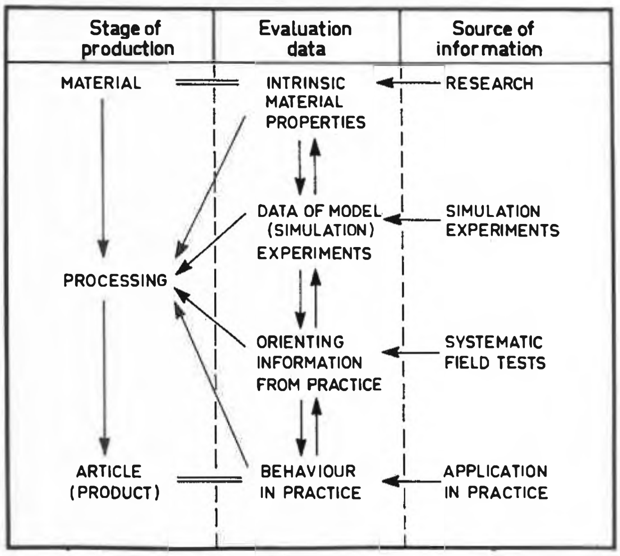


Fig. 2: Basic scheme of application research

*) In these equations the symbols have the following meaning:

ϱ = density
ΔH = heat of fusion
λ = heat conductivity
η = viscosity
ΔP = driving pressure
d = characteristic diameter
ΔT = temperature difference
γ = surface tension
Θ = wetting angle
t = characteristic time
L = characteristic length

ground is complex or even completely obscure. Examples are: wear, fatigue, surface deterioration, warpage, etc.
In these cases systematic simulation experiments or field tests are the only means to get the problem under control (e. g. by systematic variation of material composition and processing conditions) (see Fig. 2). Sometimes a "factor X" can be defined for comparative judgment of the product in simulation tests (see Table 2) [5].

Table 2: Use (product or article) properties
Dimensional stability and resistance to a factor $\varkappa$ are the criteria by which a product (article) is judged in practice.
The factor $\varkappa$ may represent a variety of influences, for most of which a testing method is available.

Factor $\varkappa$	Criterion in simulation experiment
max. service temperature	softening point, heat distortion temperature
force at low rate of loading	tensile strenth
force at high rate of loading	impact strength
force at prolonged static loading	strength durability
force at prolonged fluctuating load	fatigue resistance
aging by physical effects (recrystallization, volume shrinkage, relaxation shrinkage)	strength loss as a function of time
aging by chemical attack (stress corrosion, oxidation, hydrolysis)	strength loss as a function of time

Trends

After this general introduction I come to the trends which can be distinguished in the development of polymeric materials.
The demands of *all* categories of polymeric materials (engineering plastics, elastomers, films and membranes, fibers for reinforcements) have the following trends in common:

1. Extreme strength—in combination with
2. Sufficient toughness
3. Fatigue resistance (against periodic deformations)
4. Conservation of properties at elevated temperatures
5. Resistance against radiation and oxygen
6. Resistance against moisture, oils and chemicals
7. Flame resistance
8. Low density (high specific volume)
9. Uniformity (possibly in all directions)
10. Acceptable processability

The four different categories of polymeric materials also have their specific requirements:
Engineering plastics: high rigidity
Elastomers: conservation of rubber elasticity at very low temperatures
Films and membranes: thinness and absence of pinholes
Reinforcing fibres: very high moduli

Sometimes the requirements go parallel. For instance: in order to improve the rigidity and strength one may introduce aromatic ring structures; this also lowers the H/C-ratio which again improves the flame resistance [2]. Another example: elevation of T_g and of the crystallinity x_c work in the same direction, viz. improvement of the ultimate end-use temperature. The ultimate end-use temperature as a function of T_g and x_c meets the following correlation [2]:

$$T_{u.e.u.} \approx a T_g \left[1 + x_c \cdot \frac{T_m - T_g}{T_g}\right] \sim a T_g \,(1 + 1/2\, x_c)$$

where $a = 0.96$ for 200 hours
$a = 0.91$ for 1000 days

A third example: in order to improve the mechanical properties at high temperatures the value of T_g must be high since—as we have seen—the end-use temperature is determined by it. There is also a very evident relationship between T_g and the modulus of elasticity E.

An approximation for amorphous materials in general is:

$$E \approx 2.5 \times 10^4 \cdot T_g^2 \qquad (E \text{ in N/m}^2)$$

For crystalline polymers which are drawn in fiber-form

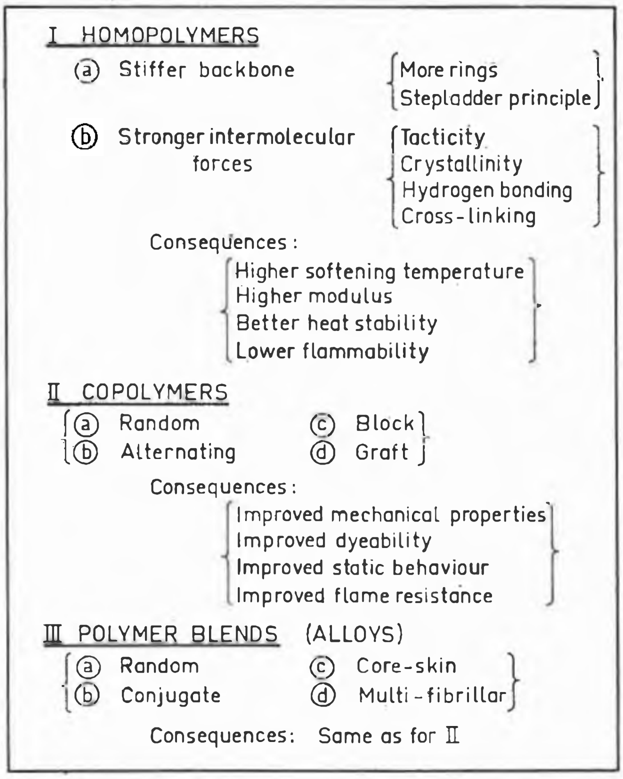


Fig. 3: Trends in Polymer Build-up

the value can be shifted to the 8-fold, depending on the crystallinity.
Sometimes, however, one requirement is contradictory to the other. A very high strength can hardly be combined with uniformity in all directions. A very high stiffness can hardly be combined with a low density. Good properties at high temperatures can hardly be combined with easy processability.
In cases of such "intrinsic contradictions" there is but one solution: *composite materials,* since this introduces new degrees of freedom. It is a matter of course that these composites have to be made out of:
a. very strong *matrix polymers*
b. very strong *reinforcing fibers*
whereas, in order to unite these two to a uniform entity, one must use
c. a very good adhering agent between *a* and *b*.
By using composite materials it is possible to improve the mechanical poperties of the matrix polymer by a factor of nearly ten.
Fig. 3 shows the trends in polymer build-up during the last 20 years. In homo-polymers the three possibilities for stiffening are: stiffer backbones, stonger intermolecular forces and cross-linking. The stiff backbone elements may be present in the monomers or they may be formed by intramolecular cyclisation.

New commercial and experimental materials.

The final part of my paper will be a short survey of some new materials, partly commercial, partly still in the experimental stage. I had to make a choice and shall restrict myself to three subjects:

1. New thermoresistant engineering plastics, poly-imides in particular.
2. New developments in fluoro-polymers.
3. New fibers for reinforcement.

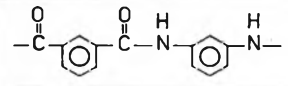
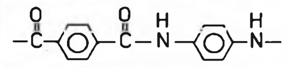
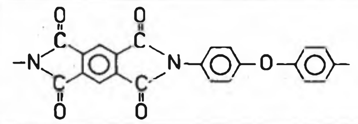
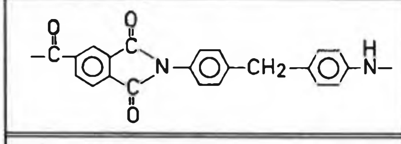
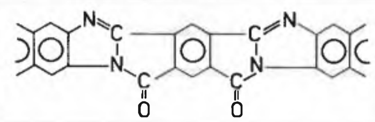
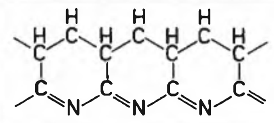
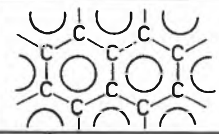
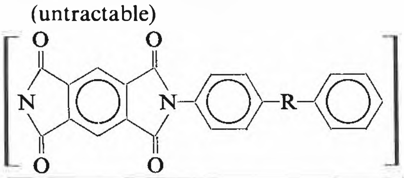
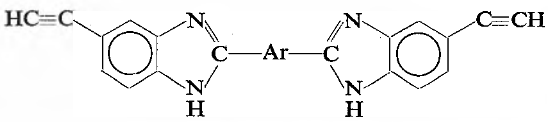
	NOMEX®
	KEVLAR®
	KAPTON®
	KERMEL®
	PYRRONE
	"BLACK ORLON"
	GRAPHITE

Fig. 4: Some thermo-resistant Polymer Classes

1. New thermo-resistant engineering plastics

Fig. 4 gives a short survey of the trends in thermo-resistant polymers; the majority of them came on the market during the last 15 years.

Table 3: New Developments in Poly-imides.

Polymeric Materials	Method of Fabrication	distortion temperature
1. Original Poly-imide (untractable) 	a. curing by cyclisation of soluble precursor (usually to film) b. curing by powder metallurgy techniques (under high temperature and pressure) applied to (pre-)polymer	360 °C
2. Crosslinked modified Poly-imides (untractable)	crosslinking by addition polymerisation via melt-processable acetylene-capped precursors 	at thermal decomposition temperature

As an interesting example for some more details I choose the developments in poly-imides [6].
The most notable representative in the class of poly-imides is the poly-pyromellitic imide, better known under its trade name Kapton® (formerly under its experimental trade name H-film). This polymer has an extremely high heat distortion temperature, viz. 360 °C. It is completely untractable, however. In order to convert this polymer to a usable shape two methods are available (see Table 3). In the first and original one a soluble (less ring-condensed) "pre-polymer" is formed into film shape which is then converted, thermally and chemically (by intramolecular cyclisation) into the poly-imide. The second method is an analogue to powder metallurgy. Under high temperature and pressure a powder of the pre-polymer is sintered in a mould into the final shape; during the sintering imide formation and cross-linking occur.
Very interesting is a new type of modified, cross-linked, poly-imide (see Table 3, lower part). Precursors are made containing acetylene groups, and having low enough molecular weights to be melt-processed. By addition-polymerization via the acetylene groups longer chains and cross-links are formed in situ (i. e. in the final shape and without evolution of gas). Also these modified cross-linked polyimides are extremely thermo-resistant.

2. New developments in fluoro-polymers [6]

The first perfluorinated polymer was poly-tetrafluoro-ethylene, PTFE, generally known under its trade name Teflon®. This polymer had a combination of properties that were unavailable in other materials: unique chemical resistance, unique thermal stability and unique low friction characteristics. It also had, however, a number of less attractive properties: due to an extremely high molecular weight it is very difficult to fabricate in complex shapes; it cannot be used under high loads, because of the ease with which the crystals deform and slip; also its surface hardness is low.

Starting from PTFE the developments of fluoro-polymers have gone into two directions: one into engineering plastics which are more easily processable, the other to fluorinated elastomers. Nearly all this work has been done in the laboratories of the Du Pont company. First the new developments in fluorinated engineering plastics. To make PTFE more processable, co-polymerization had to be applied. By well-chosen copolymerization one has succeeded in keeping the maximum use-temperature higher than 200 °C. A new experimental type is a co-polymer of vinylidene fluoride (VDF) and hexafluoro-isobutene. The co-polymer obtained has a maximum use-temperature of about 280 °C, and has a high surface hardness and good abrasion resistance.
The other trend is in the direction of chemical resistant elastomers with a broad range of use-temperatures.
Co-polymers of TFE or VDF give good use-temperatures at the high side, whereas fluorinated silicones and poly-phosphazines give very attractive possibilities in the low temperature region.
An experimental polymer hexa-fluoro-propylene oxide, which promises a good conservation of properties at both high and low temperatures is still in exploration. At present the molecular weight is still too low and the cross-linking provides difficulties.
Taken together the development of fluorinated polymers is one of the most impressive ones in polymer chemistry.

3. Fibers for reinforcements

Spectacular developments have taken place in the field of reinforcement fibers for composite materials.
One of the biggest applications is in automotive tyres.
Side by side with the improvements of the already classic materials (rayon, nylon, polyester and steel) we have seen the development of aramids (fully aromatic polyamides) and of special glass types. The other big field is reinforced engineering plastics. Next to the conventional glass fiber we have the E- and S-fiber and yarn, the high-modulus

Table 4: Fibers for Reinforcement

Materials	ϱ kg/m^3	E GPa	σ_{br} GPa	E/ϱ N/tex	σ_{br}/ϱ N/tex
cellulose	1500	25	0.75	17	0.5
nylon	1140	5	0.85	4.5	0.75
p-(ethylene-terephthalate)	1380	22	1.0	16	0.75
p-(p-phenylene-terephthalamide) (aramid)	1450	100	3.6	70	2.5
E-glass	2500	60	2.0	24	0.8
S-glass	2500	75	4.0	30	1.6
steel	7800	200	3.8	25	0.5
H M carbon	1850	325	2.0	175	1.1
H T carbon	1700	210	2.7	125	1.6
Al_2O_3 (exp.)	3970	350	2.4	90	0.6
BN (exp.)	2250	280	2.0	125	0.9
B_4C (exp.)	2520	550	3.0	220	1.2

Table 5: Typical properties of fiber-reinforced composites (fiber content 65 w-%)

Material	ϱ kg/m^3	E G Pa	σ_{br} G Pa	E/ϱ $\times 10^3$	σ_{br}/ϱ $\times 10^3$
Aramid / Epoxy	1400	62	1.24	44.5	0.89
E-glass / Epoxy	2100	35	1.10	17	0.52
S-glass / Epoxy	2100	48	1.66	23	0.79
HT-carbon / Epoxy	1560	124	1.38	80	0.66
HM-carbon / Epoxy	1660	180	1.10	108	0.65
Steel	7800	200	1.38	25.5	0.18
Aluminium	2700	70	0.56	26	0.21

Meaning of symbols:

ϱ density
E Young modulus
σ_{br} breaking strength

aramid and the different types of carbon yarns; even completely inorganic fibers such as alumina and boron compunds are under way.

Table 4 gives a survey of the most important properties of these fibers. It is clear that aramids already meet a number of demands which were considered unattainable some fifteen years ago.

Table 5 shows some properties of fiber-reinforced composites containing 35 % epoxy-resin and 65 % of fiber (in filament form) in comparison with the conventional construction materials steel and aluminium. Whereas in absolute modulus and tensile strength steel still belongs to the leaders, this is not the case in specific strength (i. e. per unit weight of material). Here the composites exceed steel as well as aluminium by far.

Final remarks and conclusions

Overseeing the developments of new polymeric materials in the last fifteen years we may state that in a number of properties the "ceiling of the possible" is almost reached. So for instance in rigidity and strenght of the polymeric fibers (aramids!) and in chemical and thermal resistance of the fluoro-polymers. For the future the challenge will remain: to find a still more extended *balance of properties* in new materials, for extreme service conditions. In this respect composite materials are promising because they open new degrees of freedom in exploration.

References

1 *H. F. Mark:* Polymers for extreme service conditions, J. Appl. Polymer Sci., Applied Polymer Symp. *35* (1979) 13.
2 *D. W. van Krevelen:* Properties of Polymers; their Estimation and Correlation with chemical structure (Sec. Ed.), Elsevier Scientific Publishing Co., Amsterdam 1976.
3 *D. W. van Krevelen:* Crystallinity of Polymers and the means to influence the crystallization process, Chimia *32* (1978) 279.
4 *A. K. van der Vegt:* Transact. Plastics Inst. *32* (1964) 165.
5 *D. W. van Krevelen:* Processing Polymers to Products, Proc. Intern. Congress, Amsterdam 1966, 't Raedthuys, Utrecht, 1967.
6 *B. C. Anderson, L. R. Bartron* and *J. W. Collette:* Trends in Polymer Development, Science *208* (1980) 807.
7 *P. Beardmore, J. J. Harwood, K. R. Kinsman* and *R. E. Robertson:* Fiber-Reinforced Composites; Engineered Structural Materials, Science *208* (1980) 833.