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Compressive strength and glass transition temperature

An empirical relation between the compressive strength and the glass transition temperature of materials composed of mainly first-row elements of the periodic table is presented. This relation indicates that flexible-chain polymers have an intrinsically low strength in axial compression, which probably disqualifies them as a reinforcement fibre in composite materials that are subjected to bending vibrations.

For an effective development of a new material it is important to have some foreknowledge of the ultimate properties that may be attained.

In the case of extended polymer chains the maximum tensile modulus is determined by the force–displacement curve of two adjacent atoms in the chain and by the cross-sectional area of the chain [1]. Moduli calculated in this way closely approach the observed values [2]. For extended linear chains (flexible as well as rigid-rod) made up of first-row atoms the theoretical modulus lies between 180 and 250 GPa. In that case the tensile curve shows elastic and brittle behaviour.

The limit for the tensile strength of a brittle, elastic solid can be derived from the force–displacement curve between two atoms. Accordingly, the theoretical strength σ_t is estimated to be [3]

$$\sigma_t \approx \frac{E}{10} \qquad (1)$$

where E is the tensile modulus. Applying Equation 1 a theoretical upper limit for the strength of about 25 GPa is derived for linear polymers. Experimentally, the fractural stress is of the order of 10 to 100 times less than σ_t.

A third important property is the strength in axial compression; commonly designated as the compressive stress at which yielding occurs. In many constructions the materials are subjected to compressive stress as in the case of bending vibrations. The phenomena which usually accompany compressive yielding of polymers are the well-known observations of kink and slip bands. These macro-distortions are large-scale manifestations resulting from the buckling of chains. In places where buckling takes place the chains are forced to adopt a very different conformation which may extend over a large part of the chain.

Below the glass transition or softening temperature, T_g, a polymer has glassy properties, above this temperature it has rubber-like properties and and near the melting point flow behaviour prevails. In the molecular interpretation of the glass–rubber transition of polymers this relaxation is associated with the onset of large-scale segmental motions in the chain. These motions are in fact large conformational changes at certain atoms in the main chain.

The amount of work required to bring about these conformational changes at compressive yielding may also be derived from the thermal energy, which becomes sufficiently large at the temperature T_g. Accordingly, such changes appear spontaneously in the material above T_g. Assuming elastic behaviour up to compressive yielding, for the compressive strength

$$\sigma_c = (2E_cW)^{1/2} \qquad (2)$$

can be written where W is the work per unit volume needed for yielding and E_c is the axially compressive modulus. The apparently common origin of phenomena such as compressive yielding and glass-transition, relating to chain flexibility and intermolecular interactions, suggests a correlation between σ_c and T_g.

In the compilation given in Table I materials have also been included which are actually three-dimensional networks in the amorphous or crystalline state. Here, however, they are regarded as three-dimensional polymers. The softening temperature cannot be properly defined for every

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TABLE I Compressive strength σ_c, Young's modulus E and T_g of materials composed of mainly first-row elements

Material	T_g (K)	E (GPa)	σ_c (MPa)
Polyethylene	148	8.5	19–25
Polypropylene	253–293	9.6	38–55
Polystyrene	373	3.5	79–110
Polyacrilonitril	378	7	76–130
Polymethylmethacrylate	353–373	3	103–124
Polycarbonate	423	–	86
Polyethyleneterephthalate	348	19.5	76–103
Polytetramethyleneterephthalate	323	–	59–100
Nylon 6	318	5	90
Nylon 66	318	5	103
Polyamide–imide	573	–	241
Poly-p-phenyleneterephthalamide	673	100	> 250
Polyvinylchloride	353	5	69–76
Polyvinylidenefluoride	323	–	62
Polychlorotrifluoroethylene	318	1.3	51–64
Polytetrafluoroethylene	160	0.4	12
Carbon fibre	2470	800	1500–2500
Graphite	3500	1000	–
Siliconcarbide fibre	1700	200	1765
E-glass fibre	1100	70	> 500
Fused quartz	1940	72	> 1100
Diamond	> 3500	1160	16500

polymer [4], because there is often a temperature range or some orientation or crystallinity effect. In addition, the axially compressive strength data are not derived from one and the same method. For fibres made of E-glass [5], carbon [6, 7], SiC [8] and poly-p-phenyleneterephthalamide [5] data are reported which are either obtained from measurements on thin filaments or from unidirectional composites with a matrix of epoxy resin and extrapolated to 100% fibre content. The other compressive strength data listed in Table I are from measurements on bulk material [9]. Presumably the σ_c value of fibres will also depend on the molecular orientation or texture: SiC fibre is paracrystalline but unoriented, poly-p-phenyleneterephthalamide fibres are paracrystalline and oriented [10]. Indeed, for carbon fibre some effect of orientation has been reported [7].

In Fig. 1 a graph is presented of log T_g against log σ_c. The equation for the regression line is given by

$$\log T_g = 1.50(0.06) + 0.54(0.03) \log \sigma_c \quad (3)$$

with T_g in K and σ_c in MPa. The standard deviation

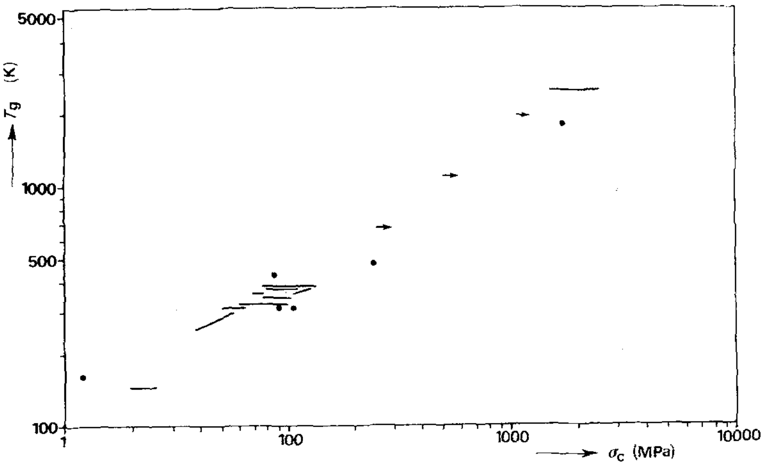

Figure 1 Glass transition temperature against compressive strength.

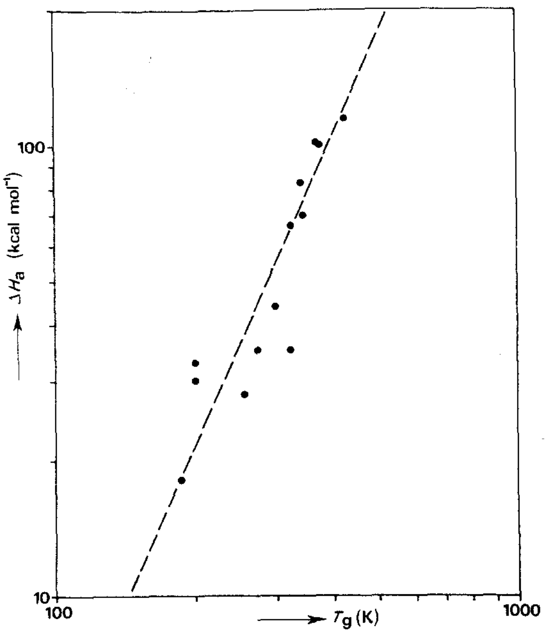

Figure 2 Activation energy against the glass transition temperature. The slope of the regression line is 2.3 ± 0.3.

of the regression coefficients is given in parentheses. Equation 3 implies that σ_c is approximately proportional to T_g^2 and supports the qualitatively formulated hypothesis of the common origin of T_g and σ_c.

The data in Fig. 1 are distributed according to the various kinds of intermolecular forces. The linear polymers consisting of flexible chains with only van der Waals interactions between the chains have the lowest values of T_g and σ_c, while covalently bonded networks like E-glass, SiC, carbon fibre and diamond show the largest values for both T_g and σ_c.

Assuming that the work for yielding W is proportional to the activation energy of the glass transition ΔH_a and that E_c equals the Young's modulus E_y, it will be shown that the relation $\sigma_c \propto T_g^2$ is consistent with empirical relations found between E_y, ΔH_a and T_g. Fig 2 gives ΔH_a as a function of T_g using the data compiled by Boyer [11] and yields the relation

$$\Delta H_a \propto T_g^{2.3} \qquad (4)$$

with a standard deviation of 0.3. From the Equations 2, 3 and 4

$$T_g \propto E_y^{0.60} \qquad (5)$$

is derived with an estimated error of 0.15. Fig. 3 gives T_g as a function of E, being for the greater part fibre moduli. Although there is an appreciable scatter, the distribution of the data is in approximate agreement with Equation 5. Apparently, the consistency of the relations between σ_c, E_y, ΔH_a and T_g originates from one dominating factor i.e. the flexibility of the polymer chain or network.

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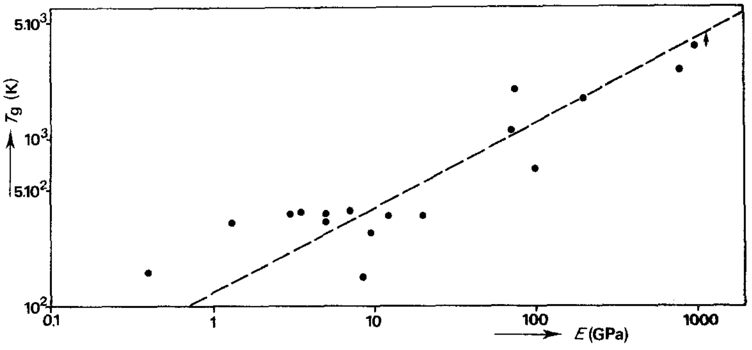

Figure 3 Glass transition temperature against Young's modulus. The slope of the broken line is 0.5.

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Thermally stimulated current studies of conduction polarization in several alkali-containing oxides

There have been several recent investigations [1–3] of alkali motion in simple glasses using the method of thermally stimulated depolarization current (TSDC). In this technique, a sample is polarized by an applied field at an appropriately chosen temperature, and quenched to a lower temperature where the polarization can be frozen-in. Then, with the field removed, the sample is heated at a linear rate as the induced current in the outer circuit is detected by depolarization. As a complement to TSDC, the method of thermally stimulated polarization current (TSPC, [4]) consists of quenching a sample, followed by heating with the field applied and measuring the current induced by the buildup of polarization. These techniques have been developed for studying orientational motion of impurity-vacancy dipoles in ionic crystals [4, 5]. Hence the TSDC peaks of alkali-containing oxide glasses were liable to be interpreted in terms of orientational depolarization of alkali-nonbridging oxygen dipoles [1, 2]. Recent work [6] on the single TSDC peak in sodium germanate glass suggests, however, that the peak is due to polarization caused by conduction itself (conduction polarization) and not to orientational motion of sodium–GeO_6^- or sodium–nonbridging oxygen dipoles.

The conduction polarization model [6] is explained shortly as follows. A conductive ion jumps by thermal activation from any given site to nearest-neighbour sites with a probability

$$\eta = \nu \exp(-H_c/kT), \tag{1}$$

where ν is an oscillation frequency of the ion within a potential well surrounded by an energy barrier H_c. When a sample is biased by an applied field, the probability distribution for a conductive ion to occupy any of the nearest-neighbour sites must be different from a distribution without a field. Such a move from a normal to a distorted distribution of conductive ions is responsible for a TSPC peak, while the reverse move produces a TSDC peak. Both techniques are said [4, 6] to give an almost identical peak temperature, T_m, for which the relationship

$$\frac{H_c}{kT_m^2} = \frac{\nu}{\beta} \exp(-H_c/kT_m) \tag{2}$$

holds, where β is the heating rate. The purpose of the present work was to re-interpret published TSDC/TSPC data of several alkali-containing oxides in terms of the conduction polarization model.

Fig. 1 shows a TSDC curve of $4Na_2O \cdot 96SiO_2$ glass polarized at around 403 K [2]. Hong and Day

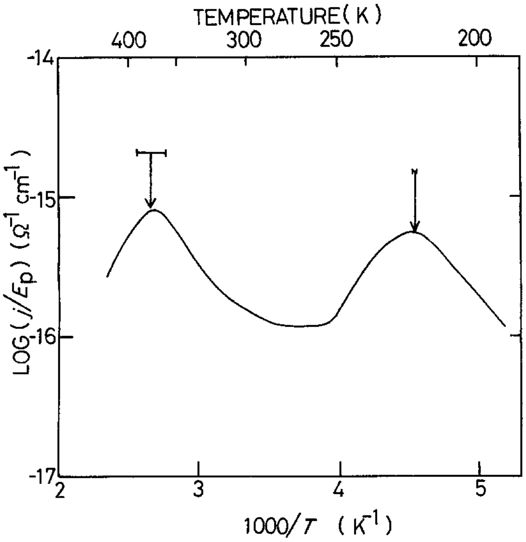

Figure 1 TSDC of $4Na_2O \cdot 96SiO_2$ glass polarized at around 403 K (Hong and Day [2]). The arrows indicate calculated peak temperatures.

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