Zbigniew Dobkowski

Determination of critical molecular weight for entangled macromolecules using the tensile strength data

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Dr. Z. Dobkowski (✉)
Industrial Chemistry Research Institute
Rydygiera 8
01-793 Warszawa, Poland

Abstract The multivariable power dependence of polymer properties on molecular characteristics (Dobkowski, 1981) has been applied to molecular weight dependence of tensile strength, and the known equation of Flory (1945) has been extended taking polydispersity of polymers into account. Constant parameters of the relevant regression equations have been calculated using experimental data on tensile strength and molecular weight averages M_n and M_w of polystyrene (PS) and polycarbonate (PC). Then, the critical molecular weight for entanglements M_c has been obtained from the following relationship:

$$A = K\sigma_\infty M_c ,$$

where A and σ_∞ are parameters of the extended Flory equation for the tensile strength, and the constant $K = 2$ is assumed for linear polymers. It has been found that M_c of injection and compression moulded PS is equal to 34000 and 37350 g/mole, respectively, while M_c of injection moulded PC equals to 5000 g/mole. The values of M_c calculated from the polymer tensile strength are consistent with published data obtained by other methods and with the computer modeling calculations. Branched polymers have only qualitatively been discussed. Dimensionless equations have been proposed for tensile strength characteristics for polymer materials.

The described procedure can be suggested as applicable to various polymers for the determination of their M_c values. However, more experimental data on another polymer materials will be necessary to support hitherto obtained results.

Key words Critical molecular weight – entanglements – tensile strength

Introduction

The concept of entanglement coupling of macromolecules in polymer condensed systems, such as melts or concentrated solutions, is commonly accepted to interpret viscoelastic properties of high molecular weight polymers (Ferry, 1980). An important parameter for entangled macromolecules is the average molecular weight spacing between entanglement junctions, i.e., the entanglement molecular weight M_e or the critical molecular weight M_c, where some polymer properties of viscoelastic nature are changed. Both M_c and M_e are interrelated and approximately

$$M_c = 2M_e . \tag{1}$$

The value of M_c is considered as a characteristic parameter for any polymer, as a kind of "passport number" (Van Krevelen, 1992). Entanglement behaviour of polymers is

correlated with parameters of their molecular geometry (Zang and Carreau, 1991; He and Porter, 1992; Fetters et al., 1994). Many mechanical and viscoelastic properties of polymers strongly depend on the value of M_e (Ferry, 1980; Graessley and Edwards, 1981; Kramer, 1983; Dettenmayer, 1983; Kramer and Berger, 1990; Sauer and Hara, 1990; Wu, 1990; Wasserman and Graessley, 1992; Cassagnau et al., 1993; Plummer et al., 1994; Nielsen and Landel, 1994). The dependence of rubbery plateau shear modulus G_N^0 on various molecular parameters, given by Graessley and Edwards (1981), has been applied for experimental determinations of M_e (Graessley and Edwards, 1981; Wu, 1990; Wasserman and Graessley, 1992; Plummer et al., 1994), as well as for computer modeling calculations of M_e (User guide, 1993). The value of M_e and the entanglement density v_e, where

$$v_e = \rho_a/M_e \qquad (2)$$

and ρ_a is the amorphous polymer density at 25 °C, both are used to distinguish between tensile and brittle behaviour in amorphous glassy polymers (Kramer, 1983; Dettenmayer, 1983; Kramer and Berger, 1990; Sauer and Hara, 1990; Wu, 1990).

A useful rule of thumb for obtaining the optimal molecular weight of a new polymer is based on the values of M_e (User guide, 1993). It states that the optimal molecular weight M_{opt} should be between 10 and 15 times the M_e value. Thus it can be written as

$$10\,M_e \qquad <M_{opt}< \qquad 15\,M_e \qquad (3)$$

(poor strength)   (difficult to process)

Several methods for estimation of M_c and M_e, described in literature, are compiled by Ferry (1980). These methods are based on (a) the dependence of zero shear rate melt viscosity η_0 on molecular weight M, (b) the integration of retardation spectrum or loss compliance, (c) the maximum value of loss component, (d) the dependence of steady state compliance J_e^0 on M, (e) the minimum value of $\tan\delta$ obtained from the dependence of $\tan\delta$ on log frequency ω.

In this paper a new method is proposed for estimation of M_c of bulk polymers that is based on experimental values of tensile strength. The general dependence of polymer properties on their molecular characteristics in the form of the multivariable power function (Dobkowski, 1981, 1988b, 1990, 1994) is applied to the tensile strength and then the value of M_c is calculated.

Theoretical backgrounds

Dependence of tensile strength on molecular weight — present status

In 1945, Flory found the following type of equation to hold for the tensile strength σ of rubber-like materials

$$\sigma = B - A/M , \qquad (4)$$

where M is the molecular weight, A and B are constants. Equation (4) has been accepted for monodisperse polymers, as well as for polydisperse polymers if $M = M_n$ (Ward, 1971; Schurz, 1974; Sauer, 1978; Nunez et al., 1982; Van Krevelen, 1990). The constant B is termed as σ_∞, where σ_∞ is the tensile strength of a polymer of infinitely high M (Sauer, 1978; Bersted and Anderson, 1990). The constant A can be derived from the relationships discussed by Bersted and Anderson (1990) as

$$A = K\sigma_\infty M_c , \qquad (5)$$

where K is a constant of values between 2 and 3 (Bersted and Anderson, 1990). Thus, Eq. (4) can be written as

$$\sigma = \sigma_\infty - A/M \qquad (6)$$

However, the validity of Eqs. (4) or (6) for $M = M_n$ in the case of polydisperse polymers is disputable (Martin et al., 1972; Kinloch and Young, 1983; Bersted and Anderson, 1990; Dobkowski, 1994). There are experimental data relating σ and M_w (Nunez et al., 1982), and observations are reported that M_w is more important for the stress-strain properties than M_n (Nielsen and Landel, 1994). Moreover, neither M_n nor M_z but only M_w can be applied as M in Eqs. (4) or (6) (Bersted and Anderson, 1990), and plots of σ as a function of M_n give multiple curves depending on the polydispersity of the samples (Martin et al., 1972). To provide a single relationship between σ and some molecular weight parameter for both narrow and broad distribution polymers, Bersted and Anderson (1990) proposed the failure property parameter

$$F_P = \phi(1 - M_T/M_n^*) , \qquad (7)$$

where M_T is the threshold molecular weight being $M_T = KM_c$, ϕ is a fraction of ineffective macromolecules of $M < M_T$, and M_n^* is the M_n of the effective fraction of macromolecules of $M > M_T$. Hence

$$\sigma = \sigma_\infty F_P . \qquad (8)$$

The failure property parameter F_P, however, has to be calculated by a trial-and-error method and it does not solve the problem of M_n or M_w in Eqs. (4) or (6) for polydisperse polymers.

The multivariable power dependence
of polymer properties on molecular characteristics

The general dependence of polymer properties on molecular characteristics in the form of multivariable power function (Dobkowski, 1981, 1988b, 1990) can be written for linear and branched polydisperse polymers as

$$P = A_P M_x^{a1} q^{a2x} G^{a3} , \qquad (9)$$

where P is a polymer property, M_x is the x-type average M, x being n, v, w, or z for number-, viscosity-, weight- or z-averages, respectively, $q = M_w/M_n$ as a measure of molecular weight distribution (MWD), G is the branching degree defined as the ratio of intrinsic viscosities of branched and linear species, A_P, a_1, a_{2x}, and a_3 are constants for the polymer property P. The term q^{a2x} represents the polydispersity correction. Thus, the problem of polydispersity and branching can be solved by the single relationship given by Eq. (9). This equation has been applied to several polymer properties, e.g., to the intrinsic viscosity $[\eta]$ to give the extended Mark-Houwink equation (Dobkowski and Brzeziński, 1981; Dobkowski, 1981, 1983, 1988b, 1990), to the zero shear rate melt viscosity η_0 to give the extended Bueche equation (Dobkowski, 1981, 1982b, 1988b, 1990), to the melt fluidity $\varphi = 1/\eta$ in the non-Newtonian range (Dobkowski, 1986, 1988a,b, 1990), to the glass transition temperature Tg (Dobkowski, 1982a, 1988b, 1990), and to the specific volume v_{sp} (Dobkowski, 1984, 1988b). Recently, Eq. (9) has been applied to the tensile strength of linear polydisperse polymers, where for linear polymers the branching degree $G = 1$. Similarly as for the Tg (Dobkowski, 1982a), the tensile strength difference $\Delta\sigma$ has been taken as the polymer property P (Dobkowski, 1994). Hence,

$$\Delta\sigma = A M_x^{a1} q^{a2x} , \qquad (10)$$

where $\Delta\sigma = \sigma_\infty - \sigma$ is an extent of the actual value of σ from the limiting value σ_∞. Equation (10) can also be written for linear polydisperse polymers as the extended equation of Flory (Dobkowski, 1994)

$$\sigma = \sigma_\infty - A M_x^{a1} q^{a2x} , \qquad (11)$$

which becomes

$$\sigma = \sigma_\infty - A M_x^{a1} \qquad (12)$$

for monodisperse polymers, i.e., for $q = 1$, where $M_x = M_n = M_w = M_z$. Usually, a_1 is assumed to be equal to -1, and then Eq. (12) becomes identical with Eqs. (4) or (6). The actual value of exponent a_1 can also be found from Eq. (10). The other constants for Eqs. (10) to (12) are calculated from appropriate regression equations using experimental data on σ, M_x and q.

Experimental

Three types of polymer materials are considered: (a) and (b) linear monodisperse and polydisperse polystyrene (PS), injection and compression moulded samples, (PS_{inj}) and (PS_{com}), respectively, (c) injection moulded samples of commercial grade linear polydisperse polycarbonate (PC).

Molecular characteristics of polystyrene (PS) samples and results of tensile strength measurements were given by Bersted and Anderson (1990) and their data have been taken for further treatment in this work. PC samples of commercial Makrolon (Bayer), Lexan (General Electric) and Bistan AW (pilot plant, "Zachem", Poland) were characterized by the gel permeation chromatography method and then the tensile strength was measured using an Instron equipment at standard conditions.

Results and discussion

Preliminary experimental data for PS_{inj}, taken from Bersted and Anderson (1990) and recalculated, are shown in Fig. 1 as a function of $1/M_n$, i.e., according to the
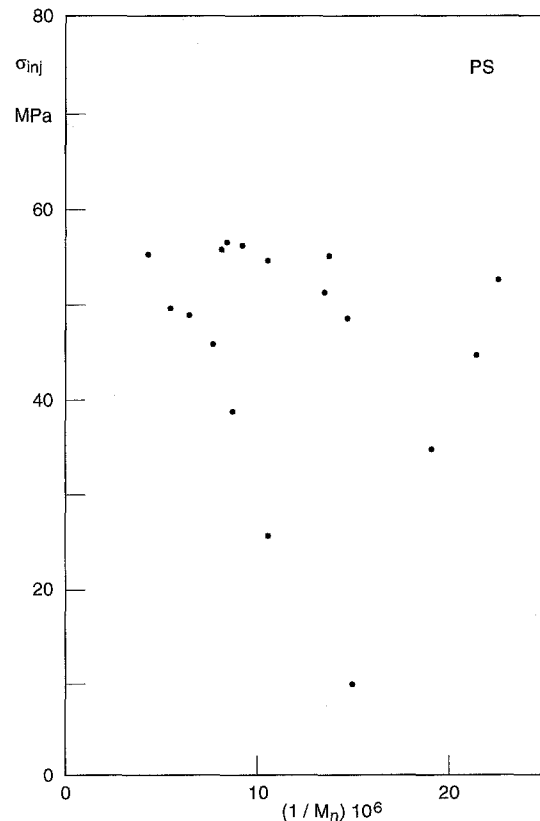

Fig. 1 Tensile strength versus $1/M_n$. Preliminary data for injection moulded PS samples, PS_{inj}

Flory equation, Eqs. (4) or (6), or Eq. (12) with $a_1 = -1$. Evidently, the dependence of σ versus $1/M_n$ is not satisfied, while the experimental data on σ versus $1/M_w$ are well correlated (Fig. 2, Table 1), both primary 17 samples (correlation coefficient $r^2 = 0.874$, $\sigma_\infty = 69.6$ MPa) and selected 11 samples after rejection of 6 outlaying data points (correlation coefficient $r^2 = 0.992$, $\sigma_\infty = 72.2$ MPa). Thus, any correction for polydispersity is not needed in the case of M_w. It means that the term of polydispersity correction for M_w in Eqs. (10) or (11) is $q^{a_{2w}} = 1$ and $a_{2w} = 0$. The same selected data have been arranged according to their polydispersity and plotted against $1/M_n$ (Fig. 3) taking the polydispersity term into account. For this purpose the extended Eqs. (10) or (11) can be written as

$$\Delta\sigma = A_x M_x^{a_1} \tag{13}$$

or

$$\sigma = \sigma_\infty - A_x M_x^{a_1} , \tag{14}$$

respectively, where

$$A_x = A\,q^{a_{2x}} . \tag{15}$$

As we have found, $A_w = A$ for M_w and the relationship of σ versus $1/M_w$ does not depend on q. For M_n, however, the value of A_n depends on q according to Eq. (15), cf. Table 2 and Fig. 4. Therefore, it is evident that

Table 1 Regression coefficients for plots of σ vs $1/M_w$

Number of data	$A \times 10^{-6}$	σ_∞, MPa	r^2
17	4.44	69.6	0.874
11	4.91	72.2	0.992

Table 2 Influence of polydispersity on the plot of σ vs $1/M_n$

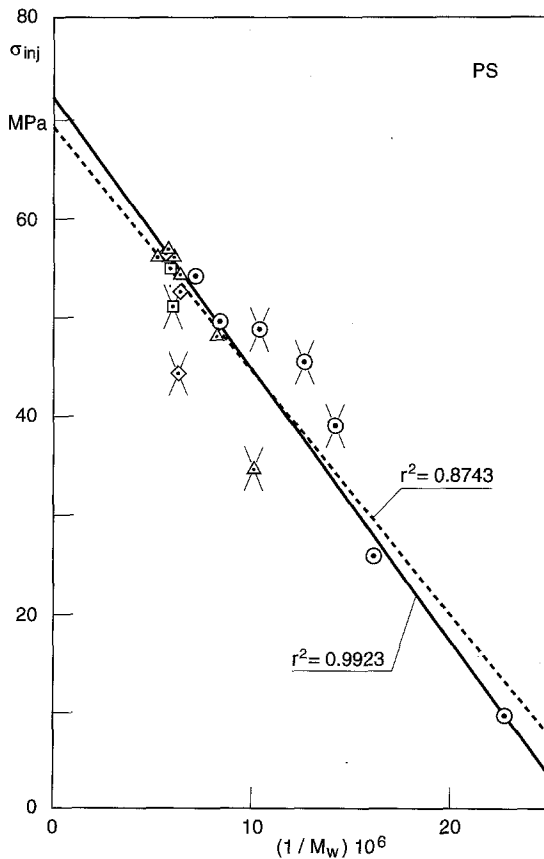| q	N	$A_n \times 10^{-6}$	σ_∞, MPa	r^2
1.12	4	4.19	71.9	0.994
2.79	5	1.59	70.9	0.966
4.12	1	1.22	(72.2)	(1)
6.31	1	0.85	(72.2)	(1)

Fig. 2 Tensile strength versus $1/M_w$. Experimental data for PS_{inj} samples of various polydispersity degree $q = M_w/M_n$: $\odot$ 1.12; $\triangle$ 2.79; $\square$ 4.12; $\diamondsuit$ 6.31. Dotted line: $N = 17$; solid line: $N = 11$ (crossed data points have been removed in this case)
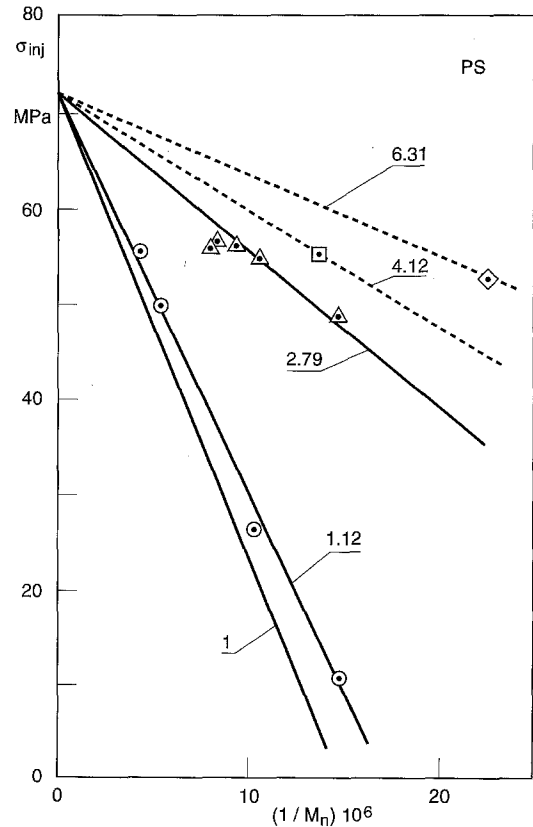

Fig. 3 Tensile strength versus $1/M_n$. Experimental data for PS_{inj} samples of various polydispersity degree $q = M_w/M_n$, cf. Table 2. Symbols as in Fig. 2. Theoretical line for $q = 1$ is drawn for comparison

Table 3 Experimental data on tensile strength σ and M_w

	After Bersted and Anderson, 1990						This work		
	(a) PS_{inj}			(b) PS_{com}			(c) PC_{inj}		
	No.	$M_w \times 10^{-3}$	σ, MPa	No.	$M_w \times 10^{-3}$	σ, MPa	No.	$M_w \times 10^{-3}$	σ, MPa
	1	78.1	10.0	1	78.1	3.1	1	31.7	48.8
	2	110	26.0	2	110	13.9			
	3	210	49.7	3	125	21.0	2	36.8	53.8
	4	249	55.4	4	141	30.7			
	5	279	54.8	5	171	34.4	3	32.7	51.1
	6	280	52.7	6	210	36.1			
	7	326	56.4	7	292	36.6	4	40.1	55.4
	8	300	55.2	8	213	35.1			
	9	213	48.7	9	292	44.5	5	30.9	51.2
	10	292	56.0	10	312	42.3			
	11	312	56.6				6	27.5	46.9

the plot of σ vs $1/M_n$ (Fig. 3) gives multiple lines, in accordance with the earlier observations (Martin et al., 1972), that depend on the polydispersity of the samples.

All experimental data on σ and M_w for polymers here considered, i.e., for PS_{inj}, PS_{com} and PC, are collected in Table 3. Then, the constants A and σ_∞ are obtained and the critical molecular weight M_c is calculated from Eq. (5), i.e.,

$$M_c = A/(K\sigma_\infty) . \qquad (16)$$

Recently, it has been suggested (Dobkowski, 1994) that the constant K, being between 2 and 3 (Bersted and Anderson, 1990), represents the chain-end effects,

Fig. 4 Influence of polydispersity degree $q = M_w/M_n$ on the values of constant A for M_n and M_w of injection moulded PS samples

similarly to the relationship for the Tg (Dobkowski, 1982a). Hence, it may be assumed that

$$K = n_e , \qquad (17)$$

where n_e is the average number of chain ends per macromolecule. Such assumption can be supported by the earlier observation of Flory (1945) that "rupture originates at the ends of molecules and hence the ease of failure (conversely the strength) should depend on the number of ends of molecules". Nunez et al. (1982) reported that "chain ends act as imperfection in the polymer network which can adversely affect the strength properties". Also, Van Krevelen (1990) indicates that "the number of chain ends is a preponderant factor" for the tensile strength. Therefore, we should have

$$K_{lin} = 2 \qquad (18a)$$

for linear polymers, and

$$K_{br} > 2 \qquad (18b)$$

for branched ones. Hence, for linear polymers Eq. (16) can be written as

$$M_c = A/(2\sigma_\infty) . \qquad (19)$$

Results of calculations of M_c are shown in Table 4. Thus, it has been found that the results are consistent with published experimental data obtained by other methods. In particular, for PS the agreement can be considered as excellent. Moreover, it seems that different levels of orientation due to various processing techniques can be distinguished for PS. In this case the injection and compression moulding techniques can be compared. The result that the M_c (PS_{inj}) is lower than M_c (PS_{com}) seems to be reasonable since during compression some portion of entanglement junctions can possibly be released. For
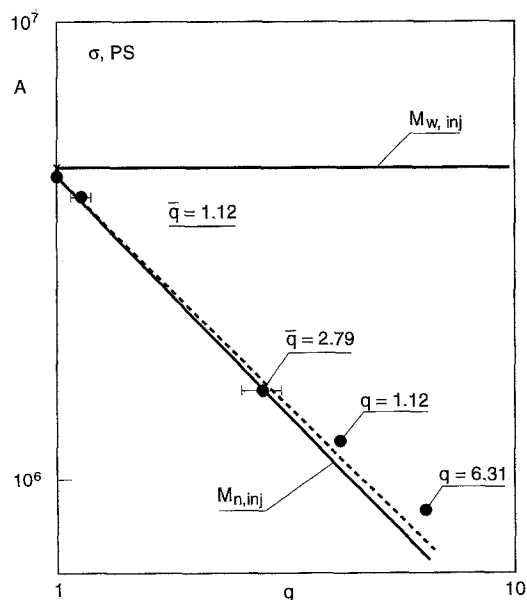
PC, a few experimental data on M_c are available in literature, however the agreement is found for the majority of quoted data (Table 4).

Moreover, our results on M_c derived from experimental data for PS and PC are consistent with theoretically predicted values using the computer modeling method, namely the Synthia Module of the Biosym Technologies polymer package (User guide, 1993). The Synthia Module uses topological information about polymers and connectivity indices for polymer repeat units derived from graph theory and properties of individual atoms (Bicerano, 1993).

Thus, the assumption that the constant K is equal to 2 for linear polymers, Eq. (18a), agrees with both experimental data and theoretical results of the computer modeling method. It may also be suggested (Dobkowski, 1994) that K is representing the chain-end effects and it is equal to the average number of chain ends per molecule, n_e (Eq. (17)).

For branched polymers rather qualitative observations have been reported that $\sigma_{br} < \sigma_{lin}$ (Wyman et al., 1965; Nielsen and Landel, 1994). Thus, the constant A in Eqs. (6) or (10)–(14) should be higher for branched species than for linear ones of the same M, i.e.,

$$A_{br} > A_{lin} \tag{20}$$

Hence, it may only be said that for branched polymers should be

$$K_{br} M_{c,br} > K_{lin} M_{c,lin} \tag{21}$$

since $\sigma_{\infty,br} = \sigma_{\infty,lin}$. The inequality (21) agrees however with the facts that a) the branched polymer has a higher number of chain ends implying $K_{br} > K_{lin}$ (Eq. (18)), and b) "the branched polymer has a fewer number of entanglements", i.e., it should have higher M_c "than the linear polymers for a given molecular weight" (Nielsen and Landel, 1994), implying $M_{c,br} > M_{c,lin}$. Thus, both factors should lower the tensile strength (cf. Eqs. (5) and (6)). The influence of various factors on the tensile strength can conveniently be analysed using the following dimensionless equations, derived from Eqs. (6) or (10)–(14) for M_w, where the polydispersity correction is not needed

$$\sigma/\sigma_\infty = 1 - [(KM_c)/M_w] \tag{22}$$

and

$$\Delta\sigma/\sigma_\infty = (KM_c)/M_w . \tag{23}$$

Equation (22) is similar in the form to Eq. (7) of Bersted and Anderson (1990). Hence, the failure property parameter given by Eq. (8) can be found and the estimation of fractions of effective or ineffective macromolecules is not needed. However, the concept of the threshold molecular weight $M_T = KM_c$ (cf. Bersted and Anderson, 1990) can be convenient for further discussion on the tensile strength of branched polymers. Moreover, the dimensionless equation for the tensile strength can be simplified and written as

$$\Delta\sigma/\sigma_\infty = M_T/M_w . \tag{24}$$

The value of the left side of Eq. (24) may be defined as the tensile strength failure index (TSFI)

$$TSFI = \Delta\sigma/\sigma_\infty , \tag{25}$$

that being an experimental criterion for tensile strength characteristics of polymer materials. The values of TSFI should be in the range from zero (for the best and ideal material) to unity (for extremely weak materials) (see Fig. 5 for samples here considered).

Table 4 Calculations of the critical molecular weight M_c

Parameters	Polymers		
	PS_{inj}	PS_{com}	PC_{inj}
Constants of the extended Flory equation (Eq. (12)) for $M_x = M_w$ and $a_1 = -1$			
σ_∞, MPa	72.2	55.7	73.7
$A \times 10^{-6}$	4.91	4.16	0.74
correlation coefficient r^2	0.9924	0.9473	0.9060
number of data points	11	10	6
Critical molecular weight M_c, g/mole			
(Eq. (19)), this work	34016	37350	5006
published experimental data		35088*	4980[1]
			3000[2]
			3580[3]
			4990[4]
			4900[5]
			4790[6]
computer modeling data: Synthia[4]		31072[4]	5586[7]

* The average of 12 published values for PS (Cassagnau et al., 1993; Ferry, 1980; Graessley and Edwards, 1981; Kramer, 1983; Sauer and Hara, 1990; Seitz, 1979; User guide, 1993; Van Krevelen, 1990; Wasserman and Graessley, 1992; Wu, 1990) in the range from 30950 to 38200 g/mole, variation coefficient 6.5%; M_c quoted or calculated from published values of M_e, Eq. (1); PS_{inj} and PS_{com} are not distinguished in the available published papers
[1] Seitz, 1979; [2] Van Krevelen, 1990; [3] Wu, 1990; [4] User guide, 1993; [5] Zang and Carreau, 1991; [6] He and Porter, 1992; [7] Eichinger, 1994
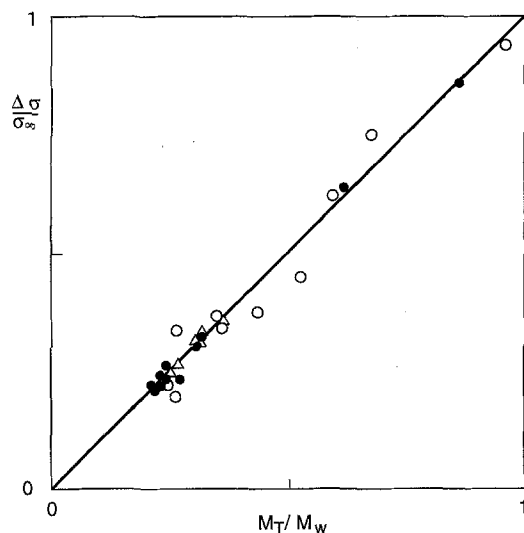
Fig. 5 Dimensionless dependence TSFI $= \Delta\sigma/\sigma_\infty$ versus M_T/M_w. ● PS_{inj}; ○ PS_{com}; △ PC

correction is not needed for the tensile strength-molecular weight dependence.

Then, it has been found that the results of calculations of the critical molecular weight for entanglements, M_c, according to the described procedure with the assumption that $K_{lin} = 2$ for linear polymers, are consistent both with published experimental data obtained by other methods and with theoretically predicted values from the computer modeling method. The value of $K_{br} > 2$ seems to be in agreement with published qualitative results on the influence of branching on the tensile strength. Thus, the assumption that the constant K represents the average number of chain ends per macromolecule seems to be confirmed.

The influence of parameters of molecular characteristics on the tensile strength can conveniently be discussed using the dimensionless Eqs. (22)–(24). The tensile strength failure index (TSFI) has been defined for tensile strength characteristics of polymer materials that should have values from zero for the best material to unity for extremely weak materials.

The procedure might be applicable for investigations of the influence of orientation due to various processing techniques on the tensile strength. The result that the M_c for injection moulded samples is lower than that for compression moulded ones seems to be reasonable since during compression some portion of entanglement junctions can possibly be released.

The described procedure can be suggested as applicable to various polymers for the determination of their M_c values. However, more experimental data on another polymer materials will be necessary to support hitherto obtained results.

Conclusions

The experimental data on three types of polymer materials (injection and compression moulded polystyrene and injection moulded polycarbonate) have been considered in this work.

It has been confirmed that the weight average M_w, not the number average M_n, should be applied for the dependence of the tensile strength σ on the polymer molecular weight M. Thus, in such case, the polydispersity

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