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On the glass transition temperature of chain-folded and chain-extended PE relating to microhardness

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Polyethylene (PE) is still nowadays one of the most common and most studied polymers. However, there is not yet full consensus among researchers about such a basic property as the value of its glass transition temperature (T_g). Values as different as around −25 and −120 °C are reported [1]. These discrepancies can be found, also, in more recent publications: $T_g = -35$ °C [2], and $T_g = -125$ °C [3]. The lack of agreement is related to the fact that PE is not commonly accessible in the amorphous state (below its melting temperature) due to its extremely high crystallization rate originating from the perfect chain structure. Even the preparation of samples with different degrees of crystallinity is not a routine task. The frequently used approach by varying the crystallization temperature and/or crystallization time is not applicable as for many other polymers. Better results can be obtained by using PE samples with different degree of branching. By introducing various amounts of chain defects in the main chain, it is possible to control the degree of crystallinity. In this way, even at constant crystallization conditions (temperature and time), one is able to prepare a series of samples with a systematic variation in the structural parameters such as degree of crystallinity, crystal size, long spacing, density, paracrystalline lattice distortions, melting temperature [4–6]. Following a given property of such a series and extrapolating to the density of completely amorphous sample, one can find support in favour of one of the two rather different values of T_g for PE.

Concerning the case of linear polyethylene (LPE), it is worth mentioning that, by means of a rather sophisticated technique, Geil succeeded in preparing fully amorphous thin LPE films [7]. These samples have been prepared on electron microscope grids for transmission electron microscopic (TEM) observations, electron diffraction (ED), and differential scanning calorimetry (DSC), as well as on glass braids for torsional braid (dynamic mechanical) analysis (DMA) [8–11]. These studies led to conclusions of fundamental character concerning the degree of order in the melt or truly amorphous polymers and the relaxation temperatures of LPE and other polyolefins [7]. On the basis of TEM, ED, DSC, and DMA, the authors [7–11] came to the conclusion that the Boyer's [12,13] concept of the two T_gs in crystallizable polymers is generally acceptable, with the low one T_g^L corresponding to the onset of a large-scale segmental motion in wholly amorphous materials; the upper one T_g^U corresponding to motion in segments constrained by nearby crystalline regions [7]. In this way, starting mostly from the torsion braid analysis [9], but supported also by the crystallization from the glassy state [7], Lam and Geil suggested two values of T_g for the truly amorphous linear PE: −83 °C, corresponding to the truly amorphous polymer, and −13 °C, corresponding to the amorphous domains constrained by adjacent crystalline regions [9]. These first direct measurements on amorphous PE using combined techniques, followed the ultra quenching experiments of Hendra et al., who used infrared (IR) measurements also reporting for the T_g of LPE a value of −83 °C [14].

Concluding these introductory remarks, it is convenient to note again that all known T_g values for PE (except the results of Hendra et al. [14] and Geil et al. [7–11]) were obtained by data extrapolation for PE with varying crystallinity values or from ethylene copolymers with various compositions [15].

As a matter of fact, the two known extreme values of T_g of PE (just below 0 °C and those around −80 and

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−100 °C), correspond to two of the main three relaxations of PE, the α, β and γ [15]. While the α-relaxation (at the highest temperature) is due to vibrational or reorientational motion within the crystals, the β-peak in LDPE is due to the relaxation of branched points, specifically of the portion of the molecule containing the side group [15]. It has been also found that, for low concentrations of side groups, the β-relaxation always occurs at about the same temperature independent of whether these groups are of methyl-, butyl-, or acetate type or chlorine atom [15].

It seems important to mention here also the recent model computations of Boyd [16] on several polymers, including PE. Performing molecular dynamic simulations, he compared the T_g values calculated from simulations with the experimentally reported ones. Boyd pointed out that, for PE, there are two distinct observable amorphous phase relaxation processes, the β and γ. According to Boyd, it is most consistent to consider the β-process as the glass transition region. However, since the γ-process is better resolved and is more prominent, some workers have preffered to consider this process to be connected with T_g. The β- and γ-values (the β-value is around −25 °C, and the γ-value is in the vicinity of −120 °C, as mentioned above), and ranges refer to measured values for these two processes: They come from a variety of low frequency dynamic mechanical and dielectric measurements. When allowance is made from an upward shift in the experimental value of T_g in the semicrystalline environment compared with an uncostrained amorphous phase, the agreement of the molecular dynamic value appears to be better with the β-process interpretation.

It has been previously demonstrated [17–22] that the microhardness technique can be used for direct or indirect evaluation of relaxation temperatures. For instance, Pereña et al. [16] reported T_g data for high and low density PE samples from direct measurements of semicrystalline samples. For this reason, these data can be hardly considered as indicative of the T_g of wholly amorphous PE.

More challenging to this respect seems to be the opportunity for evaluating T_g from wholly amorphous PE again indirectly, as in the majority of cases [1,15], by using a recently derived linear relationship between microhardness (H) and T_g of completely amorphous polymers [23] and from microhardness model studies [24] on PE samples. It is found that H linearly increases with the rise of crystallinity, as reported for many polymers [21]. From the straight line of the plot of H vs density (ρ) for differently branched PE samples, the H value for the completely amorphous PE ($\rho = 0.855$ g/cm^3 [1]) was evaluated [24]. The obtained H value was further used for the calculation of T_g of PE by means of the linear relationship between H and T_g for completely amorphous polymers.

On the basis of the data for 14 amorphous homo- and copolymers, the following relationship has been derived [23]:

$$H = 1.97T_g - 571 \text{ (MPa)} \qquad (T_g \text{ in K}) \tag{1}$$

By using Eq. (1) and extrapolating H for completely amorphous PE ($\rho = 0.855$ g/cm^3 [1]) one obtains a value of $T_g = -23$ °C. This value can be considered as the T_g of completely (wholly, truly) amorphous branched PE [25].

The fact that Eq. (1) contains a negative term reflects an important peculiarity of the proposed relationship between H and T_g. Before disclosing this peculiarity let us remind some restrictions of the technique used for evaluation of H, namely the fact that in order to use it one needs a substance which is solid at the temperature of measurements, i.e. the sample has to be capable to form a well defined impression with reliably measurable sizes. In case the sample is soft at ambient conditions, one assumes, according to the common practice [21], its H-value to be zero, which does not seem to be the best solution, particularly for complex systems containing such soft component and/or phase.

In contrast to this situation, Eq. (1) allows one to account for the contribution of the soft component and/or phase to H of the overall complex system, because it covers very large temperature interval including regions where the soft component is liquid-like. In such cases, the contribution is accounted by the 'reducing effect' of this component and/or phase in which the solid particles are immersed. As a matter of fact, the latter 'float' and thus, they are not able to experience their real microhardness. The reduction of H depends on viscosity of the soft matrix and this effect can be quantitatively accounted by Eq. (1) through the respective value of T_g. In this way, the above-mentioned shortcoming of the used technique for H measurements, is compensated to some extent.

The fact that Eq. (1) covers quite a large range of temperatures and thus includes polymers with T_g value far below room temperature (RT) results in the negative term. For the same reason, for very soft materials (with $T_g < \text{RT}$) the calculation of H according to Eq. (1) leads formally to negative numbers, which by no means should be considered as characteristics of such soft materials. These H values are only an intermediate step, and a useful tool in the same time, towards the quantitative accounting of the contribution of the soft, liquid-like component and/or phase to the overall microhardness of complex systems comprising such soft component and or/phase.

The goal of this short communication is to apply the same approach [24,25] for the evaluation of the T_g value of the amorphous regions of PE comprising extended-chain or chain folded crystals. This opportunity is offered by the recently [26,27] published data on morphology and microhardness characterization of chain-extended and chain-folded PE of two series with very wide apart molecular weights (150,000 and 2 millions).

The PE samples used were Rigidex 9 (B. P. Chemicals Ltd, Grangemouth, UK) and Hifax 1900 (Hercules Powder Co. Inc., Wilmington, DE, USA). Hifax has a molecular weight in excess of two million, whereas $M_n = 11.700 \times$ g/mol and $M_w = 155.000$ g/mol for Rigidex [26,27]. Initially, both, the standard and the high molecular weight materials have been prepared as 1-mm thick moulded sheets at atmospheric pressure by slow cooling from the melt. Portions of such sheets have been wrapped in aluminium foil, immersed in a glycerine bath at 130 °C for various periods of time, and subsequently quenched in ice water [26,27]. High pressure annealing has been performed at 5.35 kbar for 15 min and various temperatures according to the procedure of Bassett and Carder [28]. The high-pressure crystallization consists of cooling from the melt at 260 °C and 4.95 kbar at a rate of ~ 1 K/min^{-1}.

Density values to ± 0.004 g/cm^3 have been obtained at 23.0 °C with a column of mixed toluene and carbon tetrachloride [26,27]. Hardness has been measured from the residual impression using a Vickers diamond and various loads to correct for the instant elastic recovery [26,27].

The logarithmic H increase with annealing time at a constant annealing temperature has been discussed in terms of the crystallinity and crystalline lamellar thickness changes [26]. Unusually high hardness values have been obtained for samples crystallized or annealed at high pressure as a consequence of the resulting high degree of crystallinity and large crystalline lamellar thickness values [26].

Of interest for the purposes of the present study are the reported data on microhardness and density, ρ, of chain-folded PE samples with various molecular weight as well as those with extended-chain crystallites again from the two types of PE [26].

Fig. 1 shows the relationship between H and density of chain-folded PE samples with the two molecular weights studied. One can see that the data points define two straight lines arising from the two molecular weights samples. Extrapolation to $\rho = 0.860$ g/cm^3 [26] results in two H values for the completely amorphous samples. This ρ_a value is slightly higher than the usually reported one of $\rho = 0.855$ g/cm^3 [1]. The H_a values obtained for the low molecular weight and high molecular weight samples are -153 and -35 MPa, respectively. These values, as mentioned above, do not have any physical meaning, but they can be useful for further calculations.

By means of Eq. (1) and the above data for H_a one can now evaluate the T_g values of the two types of samples. The obtained values are as follows: $T_g = -60$ °C for the samples with lower molecular weight and $T_g = -1$ °C for the PE with higher molecular weight.

Before commenting these results and particularly their comparison with the analogous result for the extended-chain crystals, it is noteworthy that the extrapolation of these straight lines (Fig. 1) for the microhardness of an ideal PE crystal (with $\rho \cong 1$ g/cm^3 [1,25]) furnishes values of $H_c^{\text{ideal}} = 140$ MPa for the samples with lower molecular weight and $H_c^{\text{ideal}} = 110$ MPa for the samples with higher molecular weight. Both values are close to reported ones for the same samples using for the extrapolation other structural parameters [25]. However, they deviate notably from the H_c value for infinitely thick crystals derived from the dependence of crystal hardness on crystal thickness for melt crystallized PE samples ($H_c^{\infty} \sim 170$ MPa) [29]. What seems to be relevant, is the fact that the results obtained for H_c^{ideal} are in reasonable consonance with the extrapolation done for H_a—the microhardness of the completely amorphous regions of PE with chain-folded crystals.

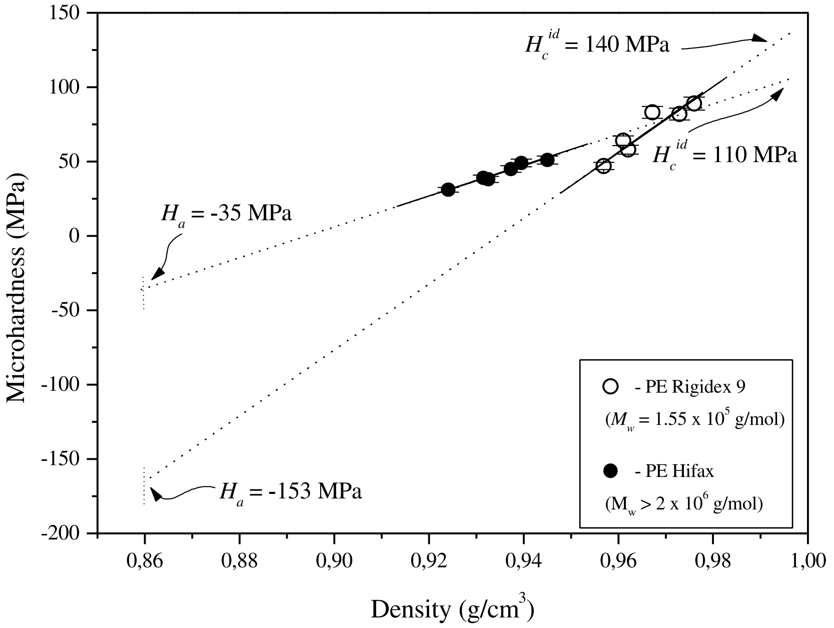

Fig. 1. Plot of microhardness as a function of density for chain-folded PE with two molecular weights: (○)—$M_w = 1.55 \times 10^5$ g/mol; and (●)—$M_w > 2 \times 10^6$ g/mol.

Let us next present similar data for the samples characterized by chain-extended crystals (see Fig. 2). First of all, one has to note that the extrapolation of the straight line in this case to $\rho = 1$ g/cm^3 leads to a value of $H_c^{\text{ideal}} = 121$ MPa which is rather close to the obtained for the chain-folded samples (Fig. 1, Table 1). What is remarkable in this respect is the observation that one of the samples (with lower molecular weight) exhibits a higher experimentally measured value ($H^{\text{exp}} = 126$ MPa) than the extrapolated one but still being below those described above (Table 1) and other values for H_c^{ideal} derived from thermodynamic calculations [29].

From the extrapolation of the straight line in Fig. 2 for H_a, one obtains for $H_a = -14$ MPa which is the highest value among the studied samples (Table 1). The application of this H_a value to Eq. (1) leads to a glass transition temperature of the amorphous regions in the chain-extended PE samples of $T_g = 10$ °C.

Fig. 2 has a peculiarity related to the number of experimental points and their mutual positions as well as to the fact that these points define not only one extrapolation line, which makes the extrapolated values not quite reliable.

The reason for the very close to each other placement of the experimental points originates from the fact that PE samples, obtained as a result of the used treatment, are characterized by an extremely high density and crystallinity, respectively, particularly for the chain-extended crystals, and what is more, this situation can hardly be changed. This grouping of the few experimental points can, as a matter of fact, define another straight line with opposite slop in comparison with the shown one on Fig. 2, as it was demonstrated by the computer treatment of the data. We only selected the more logical line.

What the relationship between microhardness and density, being the fundament of the present study, concerns, it should be remind that an earlier study [21] of the hardness dependence on density of melt crystallized PE revealed that for crystallinities larger than 50%, the plastic strain is dominated by the deformation modes of the crystal. In another systematic study on the relationship between H and density it has been found a well defined relationship in a wide density range for various types of PE [30]. In a narrower density ranges the same relationship has been successfully used for extrapolation purposes [24].

By the way, the linear relationship between H and ρ for narrower density range (covering the density values of samples with the same chemical composition) is observed also in the present case for PE samples with chain folded morphology (Fig. 1). A perfect linear relationship between H and ρ has been reported for thermodynamically miscible blends of poly(methyl methacrylate) (PMMA) and poly(vinilydene fluoride) (PVDF) [31]. What is more, very recently [32] it was demonstrated that the calculated by means of Eq. (1) H values for the amorphous PMMA/PVDF blends with various composition, but known T_g values, are practically the same as the measured ones (difference of a couple of percents).

The quite obvious relationship between H and ρ is not surprising since the density is a packaging sensitive parameter and the microhardness depends primarily on the packaging density of the substances. This statement is supported by the observation [33] that microhardness and density have the same temperature dependence in sense

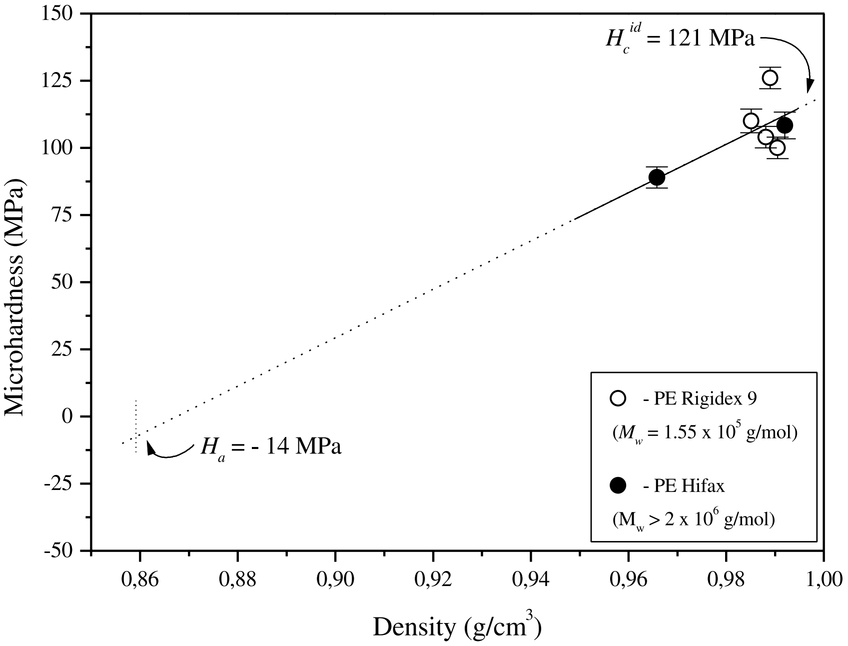

Fig. 2. Plot of microhardness as function of density for chain-extended PE with two molecular weights: (○)—$M_w = 1.55 \times 10^5$ g/mol; and (●)—$M_w > 2 \times 10^6$ g/mol.

Table 1
Molecular weight M_w, extrapolated H_a and H_c^{ideal} values from the density dependence of microhardness (Figs. 1 and 2) and T_g values calculated by means of Eq. (1) for chain-folded and chain-extended PE

Sample designation	M_w (g/mol)	H_a (MPa)	H_c^{ideal} (MPa)	T_g (°C)
PE-Rigidex 9 (chain-folded)	1.55×10^5	−153	140	−60
PE-Hifax (chain-folded)	$>2 \times 10^6$	−35	110	−1
PE-Rigidex 9 and Hifax (chain-extended)	1.55×10^5, $>2 \times 10^6$	−14	121	10

that both of them change linearly with temperature below and above T_g of completely amorphous polymers. The change in the slopes of the straight lines takes place at the same temperature defining the respective T_g value (for the glassy polystyrene and PMMA the T_g values obtained from H and ρ temperature dependencies differ only by 1 and 3 °C, respectively [33]). Obviously, this observation is related to the fact that glassy polymers, regardless of their chemical composition, behave in the same way with respect to their thermal expansion. For 8 amorphous polymers it has been reported [34] that below their T_g their thermal expansion coefficients are between 2.1×10^{-4} and $2.7 \times 10^{-4}\ K^{-1}$ but for the majority of them this interval is even narrower, between 2.5×10^{-4} and $2.7 \times 10^{-4}\ K^{-1}$ [34].

An additional support in favor of the close relationship between microhardness and density originates from crystalline polymers (PE). The inherent relationship between H and packing density of the structural elements of solids was demonstrated by the experimentally derived linear equation relating H with a parameter accounting for the perfection of crystallites (the paracrystalline lattice distortion parameter) [24].

Regarding the reliability of the approach used for the evaluation of T_g and its comparison with other methods, it should be mentioned also that its applicability has been demonstrated for various systems (homopolymers, copolymers, polymer blends of thermodynamically miscible and non-miscible partners) [35].

What seems worth mentioning at this point is the fact that the obtained in the present work T_g values could hardly be compared with any other values resulted from other methods for the same samples for a simple reason. It is well known, that in order to register a T_g by some of the commonly used techniques it is necessary to have relatively large, spatially well-defined regions of the amorphous phase. This is hardly the case for such an extreme situation when the amorphous phase amounts only ca. 5%. It likes reasonable to accept that this amorphous 'phase' is distributed as defects in the largely dominating crystalline phase. For this reason, the fact that the suggested approach via Eq. (1) offers the possibility to get an idea about the T_g values of highly constrained and small in amount amorphous phases in semicrystalline polymers could be considered as advantage, as compared to the well known and widely used techniques.

At this stage it is important to stress that the reported in the present study T_g values (Table 1) should, by no means, be considered as typical ones for the 'common', linear PE, since they characterize amorphous PE chains being extremely high constrained particularly in the chain-extended samples. The calculated T_g values reflect sooner the fact that such chains are distinguished by strongly restricted flexibility, contrasting the situation of the free, non-constrained chains. Only taking into account this consideration one can explain the relatively large differences in the T_g values obtained (Table 1).

The data on T_g (Table 1) support the statement about the effect of flexibility restrictions in the amorphous areas on the T_g of a particular sample as pointed out by Geil [7]. In agreement with this concept, the lowest T_g value in the present series of samples can be expected for the chain-folded samples with the lower molecular weight ($T_g = -60$ °C) followed by the higher molecular weight ones with the same morphology ($T_g = -1$ °C) and the highest one ($T_g = 10$ °C)—for extended-chain samples of both types.

For a better understanding of this unusually high T_g value in the last case we have to recall that all the chain-extended samples are distinguished by an extremely high degree of crystallinity (above 90%, typically between 93 and 96%) as evaluated from density measurements [25]. There is no doubt that in samples with such a tiny amount of amorphous fraction the amorphous chains (if any) are in an extremely constrained state having poor flexibility and thus demonstrating a relatively high T_g value as compared to the unconstrained amorphous chains.

In conclusion, the microhardness technique allows not only a rather uncomplicated and at the same time precise determination of T_g when the temperature dependence of H is followed [21,25], but also helps to estimate the glass transition temperature of the amorphous areas in semicrystalline polymer via exploiting the proven relationship between T_g and H. In addition, this approach demonstrates the crucial role of the flexibility restricting factors for the T_g value of a semicrystalline material.

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