ON THE DERIVATION OF MICROHARDNESS OF AMORPHOUS BLENDS OF
MISCIBLE POLYMERS FROM GLASS TRANSITION TEMPERATURE VALUES

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Based on microhardness (H) data measured at room temperature, for a large number of non-crystallizable and crystallizable polymers prepared in the amorphous state, a linear empirical correlation between H and the glass transition temperature, T_g , was recently derived [1]:

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

This expression allows one to calculate the H value of an amorphous homo- or copolymer starting only from its T_g value, i.e. without performing of any experimental measurement.

Equation 1 has certain limitations: (i) it was derived only using measurements carried out at room temperature; thus the calculated values refer only to room temperature (as a matter of fact, a modification of Equation 1 was proposed later accounting for any temperature of measurement below the T_g of the respective polymer) [2]; (ii) Equation 1 can only be applied to polymers characterized by dominating single C – C or C – O and C – N bonds in the main chain; (iii) it is derived on the basis of one-phase and *one-component* systems.

Taking into account the above peculiarities and more specifically the last one, it looked challenging to check whether Equation 1 can be applied to one-phase (amorphous *one*) and *two-component* systems, e.g. blends of thermodynamic miscible (not only compatible!) polymers. If this were the case, one could evaluate the T_g value of the blend for any composition by means of Gordon and Taylor Equation [3], using additionally Equation 1. In this way one could calculate the microhardness of the blend without performing any additional experimental measurement. The aim of the present short communication is to demonstrate that one can derive the microhardness of any polymer blend of miscible partners from T_g values by simple use of both, Gordon – Taylor's and the hardness Equation 1.

A first verification of this concept can be straightforwardly done using the experimental T_g data of blends of atactic poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVDF) in the amorphous state measured in our laboratory some time ago [4]. In our study the microhardness, the T_g (from differential scanning calorimetry, DSC) and the density ρ of the amorphous (according to X-ray analysis) were derived. It is known [5, 6] these two polymers are miscible; so far PVDF is not in a crystalline state. In addition, regarding the complete miscibility it was concluded that all the blends studied were characterized by only one T_g value on the DSC traces [4].

Starting by the T_g value of the neat PMMA (T_g^{PMMA} 393 K, as reported in [4] which corresponds to the upper limit of the commonly accepted values [7]) and that of the neat PVDF ($T_g^{\text{PVDF}} \sim 233$ K [5]), the T_g values of the various blends (T_g^B) of PMMA/PVDF were calculated using Gordon and Taylor equation [3]:

$$T_g^B = [T_{g1}(\phi_i) + kT_{g2}(1 - \phi_i)] / [\phi_i + k(1 - \phi_i)] \quad (2)$$

where T_{g1} and T_{g2} are the T_g values for PMMA and PVDF, respectively, and k is a constant equal to 1.70. The calculated data are presented in Table I together with the experimentally measured ones by DSC [4].

Using the calculated T_g values of the PMMA/PVDF blends from Equation 2 the microhardness values of the blends H^B were derived employing Equation 1. These values are listed in Table I together with the experimental data H^{exp} for the same blends as reported in [4].

From Table I one observes that the agreement between the calculated (using Equations 2 and 1) H^{cal} and the experimentally measured values H^{exp} [4] for the same blend compositions is not as good as expected.

What may be the reason for the discrepancy found between the calculated and experimental values (Table I)? A possible explanation could be related to the appearance in the samples of a harder (pseudo crystalline) phase during the sample preparation (dissolving in a common solvent, precipitation, hot pressing at 190°C and quenching in cold water [4]). This assumption is also supported by the density data from ref [4] (see Table I). For the neat PVDF a density value of 1.740 g cm⁻³ is reported while in the literature a value for the fully amorphous PVDF (ρ_a) of 1.68 g cm⁻³ can be found [6]. This difference in ρ_a suggests that some ordering in the system may have taken place during the sample preparation. Using the value of $\rho_c = 1.93$ g cm⁻³ for the completely crystalline PVDF [6] (which corresponds to the α -, also called type I-modification, i.e. crystallization from melt) one could estimate an apparent degree of crystallinity $w_c = \frac{\rho_c}{\rho} [(\rho - \rho_a) / (\rho_c - \rho_a)]$ for the sample with $\rho = 1.74$ g cm⁻³, leading to $w_c = 0.25$.

At this stage it is to be noted that, as mentioned above, all the samples under investigation do not exhibit any X-ray crystallinity [4]. For this reason the observed increase of ρ can be considered as a densification process of the glass. As reported recently for glassy poly(ethylene terephthalate) such a change in the density of the glass has a tremendous effect on the microhardness [8].

Based on the fact that all the samples (Table I) were prepared in the same manner [4], one can assume that the corresponding PVDF fraction in each blend is characterized by the same

“degree of crystallinity” (25%). This finding allows us to consider formally the blend samples under investigation (Table I) as two-phase systems (with exception of the neat PMMA). In case of such blends the microhardness can be calculated by means of the additivity law [9] as:

$$H^B = \varphi[H_c^{PVDF} w_c + H_a^{PDVF} (1 - w_c)] + (1 - \varphi)H_a^{PMMA} \quad (3)$$

where φ is the mass fraction of PVDF in the blend, and H_c and H_a – the microhardness values for the completely crystalline and fully amorphous samples, respectively.

By combination of Equations 3 and 1 one obtains:

$$H^B = \varphi[H_c^{PVDF} w_c + (1.97T_g^{PVDF} - 571)] + (1 - \varphi)(1.97T_g^{PMMA} - 571) \quad (4)$$

H_c^{PVDF} can be easily evaluated using the extrapolated microhardness value for the neat PVDF (with $w_c = 25\%$) of $H = 0$ MPa [4] according to:

$$H = H_c^{PVDF} w_c + (1 - w_c)(1.97T_g^{PVDF} - 571) \quad (5)$$

For $w_c = 25\%$ and $H = 0$ MPa a value of $H_c^{PVDF} = 336$ MPa is obtained. Using this value of H_c^{PVDF} and letting $T_g^{PVDF} = 233$ K and $T_g^{PMMA} = 393$ K (Table I), one can calculate by means of Equation 4 the microhardness of the studied blends. The values obtained are summarized in Table I as H^{cal} from Equation 4.

After taking into account the fraction of the densified PVDF one observes now a better agreement between the experimental and calculated results.

The suggested treatment considers formally the PMMA/PVDF blends as a three-phase system – two amorphous and one “crystalline” (PVDF). Let us try next to calculate the H^B values taking into account the real situation, i.e. (i) the two components are completely miscible in the amorphous state, and (ii) this amorphous phase displays only one T_g . Then H^B will be:

$$H^B = \varphi_c H_c^{PVDF} + (1 - \varphi_c)(1.97T_g^B - 571) \quad (6)$$

where φ_c is the mass fraction of the “crystalline” PVDF phase and $(1-\varphi_c)$ of the amorphous two-component blend.

Using the values for T_g^B as derived from Gordon and Taylor equation (Equation 2) one obtains using Equation 6 the values of H^B listed also in Table I on its last column. A relatively good agreement with the reported [4] H^{exp} values can be observed (Table I). In specific cases the agreement is even better than in the previous three-phase model treatment (according to Equation 4). Fig. 1 summarizes the comparison of the experimental H values and the calculated ones in different ways. It is evident that the experimental values for H are in good agreement with those calculated by means of Equations 4 and 6, i.e. taking into account the densifying effect (Fig. 1, solid line). This observation contrasts to the case when no account for the densification effect is made (see Fig. 1, dotted line).

The most serious exception in this respect is the blend 75/25, for which much better value (see the value in brackets, Table I) is obtained if one uses the measured $T_g = 359$ K (Table I) instead of the calculated by means of Equation (2) value. This difference can be explained by a possible higher „densification“ of this particular sample which results in a T_g increase as reported for many polymers [7].

The above result allows one to conclude that the amorphous blends of miscible partners can be treated in the same way as the amorphous neat homo- and copolymers regarding the relationship between their glass transition temperature and microhardness. What is more, it is not necessary to measure experimentally not only their microhardness but also their T_g values for any blend composition because these values can be evaluated by means of Gordon and Taylor equation.

Particularly striking in the present results (Table I) is the observation that the calculated H data for the discussed blends do not significantly depend on the model applied, i.e. if the amorphous blend is considered as a two-phase one (or even as a three-phase one) or as one-phase two-component system. The only parameter that counts is the mass fraction of each component and/or phase and the respective T_g value. It is noteworthy that a similar behaviour has been observed between blends of homopolymers and copolymers prepared from the same monomers [9, 10].

In conclusion, from the present results and from previous ones [9, 10], it is shown that the microhardness of multi-component and/or multiphase polymer systems depends on the chemical composition of the constituting elements expressed in their T_g value in addition to their mass fraction in the system. The verification of the described approach, namely the application of Equation 1 *via* Equation 2 using other amorphous blends of miscible polymers, is under progress.

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TABLE I Composition of PMMA/PVDF blends, their density ρ , glass transition temperatures T_g and microhardness H values as measured (ref. [4]) or calculated by means of Equations 2 and 1, 4, 6, respectively.

PMMA/ PVDF (by wt.)	T_g^{exp} (K) [4]	T_g^{cal} (K) Eq. 2	ρ (g.cm ⁻³) [4]	H^{exp} (MPa) [4]	H^{cal} (MPa) Eq. 1	H^{cal} (MPa) Eq. 4	H^{cal} (MPa) Eq. 6
100/0	393	-	1,1838	212	201	203	203
75/25	359	336	1,2766	160	91	152	106 (148)
55/45	337	340	1,3701	125	100	117	125
50/50	331	333	1,3901	107	84	102	113
45/55	325	325	1,4190	103	69	92	106
40/60	319	317	1,4437	70	53	81	93
25/75	293	291	1,5462	53	2,3	52	65
0/100	233	-	1,7400	0 (extrapolated)	-112	1	0

Figure captions

Figure 1 Plot of microhardness vs. density: - experimentally measured data from ref. 4 (●);
calculated data from Equations: - (1), (□); - (4) (○) and - (6) (△).