

On the application of the “rule of mixture” to microhardness of complex polymer systems containing a soft component and/or phase

S. Fakirov

Received: 22 July 2004 / Accepted: 30 May 2006 / Published online: 25 January 2007
© Springer Science+Business Media, LLC 2007

Abstract The main goal of this work is to find a reasonable explanation for the frequently reported drastic deviations from the “rule of mixture” applied for calculation of the overall microhardness, H , of complex polymer systems comprising a soft, (with a glass transition, T_g , or melting, T_m , temperatures below room temperature) component and/or phase. According to the common practice, the contribution to H of the soft component and/or phase, H^s , is considered as $H^s = 0$, which results in extremely large differences between the measured and calculated H values for systems comprising more than 20–25 wt% soft component and/or phase. For such systems a different deformation mechanism during indentation process is postulated, namely “floating” of the solid particles in the soft component and/or phase, in addition to their plastic deformation. The contribution of the “floating effect” to the overall H is accounted for by the empirically derived relationship $H = 1.97 T_g - 571$. Using the reported data on H and T_g for homopolymers, blockcopolymers and blends, the H values are recalculated and a good agreement with the experimentally measured values is found. A modified additivity law is suggested, which contains a term accounting for the contribution of the soft component and/or phase to the overall microhardness via the

relationship between H and T_g ; its application results in much smaller differences between the measured and calculated H values.

Introduction

Recent years have seen the microindentation hardness technique gaining increasing application in the characterization of the structure and morphology of polymers [1–5]. The method uses a sharp indenter that penetrates the surface of the specimen upon application of a given load at a known rate. Pyramid indenters are best suited for indentation tests. Here the hardness, in principle, does not depend on the size of the indentation and the elastic recovery is minimized in comparison to other indenters. During an indentation test the response of a polymeric material is initially elastic. When the stresses exceed the elastic limit, plastic flow occurs and a permanent deformation arises. At this stage, the plastic yield stress and the elastic modulus govern the elasto–plastic response to indentation [6]. When the load is removed, the indentation depth recovers elastically while the diagonal of the impression remains nearly unaltered [7]. The complicating effects of viscoelastic relaxation are usually minimized by measuring the indentation diagonal immediately after the load release [8]. The size of the permanent area of impression has been shown to depend on the arrangement and structure of the microcrystals and the specific morphology of the polymeric material [8, 9]. From a mechanical point of view, the polymer may be regarded as a composite consisting of alternating crystalline and disordered

On leave from Laboratory on Polymers, University of Sofia, 1126 Sofia, Bulgaria.

S. Fakirov (✉)
Centre for Advanced Composite Materials and Department
of Mechanical Engineering, The University of Auckland,
92019, Auckland, New Zealand
e-mail: fakirov@chem.uni-sofia.bg

elements [8]. An earlier study of the hardness dependence on the density, ρ , of melt crystallized polyethylene (PE), revealed that for crystallinities larger than 50%, the plastic strain is dominated by the deformation modes of the crystals [9].

It is important to note in these introductory remarks that, like many mechanical properties of solids, microhardness obeys the “rule of mixture”, frequently also called the “additivity law” (further referred to only as additivity law):

$$H = \sum H_i \phi_i \quad (1)$$

where H_i and ϕ_i are the microhardness and mass fraction, respectively, of each component and/or phase. This law can be applied to multicomponent and/or multiphase systems provided each component and/or phase is characterized by its own H . Equation (1) is frequently used in semicrystalline polymers for one or other purpose operating with the microhardness values of the crystalline, H_c , and amorphous, H_a , phases, respectively. This relationship is of great value because it offers the opportunity to characterize micromechanically components and or phases of a system, which are not accessible to direct measurement.

Application of the additivity law (Eq. (1)) presumes a very important requirement—each component and/or phase of the complex system should have a T_g or T_m values above room temperature (at which the indentation is performed) and thus be capable of developing an indentation impression after the removal of the indenter. If this is not the case, the assumption $H_a = 0$ for the soft component and/or phase does not seem to be the best solution, although it is frequently made.

The assumption $H_a = 0$ would mean that the soft component and/or phase (with a T_g or T_m temperatures below room temperature and not displaying its own indentation impression) has only a “diluting effect”. The role of such a component and/or phase in the formation of the overall H of the complex system is not only in the “diluting effect”. It creates a completely different *deformation mechanism* (in addition to the plastic deformation of the solid component and/or phase) as compared to the deformation behavior of complex systems non-comprising a soft component and/or phase. The deformation mechanism of the entire system is changed in such a way that the system does not obey anymore the additivity law (Eq. (1)).

It has been demonstrated that many semicrystalline polymers, copolymers and blends obey the additivity law [1]. Exceptions, such as blends of high density (HD), polyethylene (HDPE) with polypropylene (PP)

have been explained by a peculiarity in the morphology and characteristics of the crystallites formed (mostly related to the crystal sizes, surface free energy, and others) [1, 10].

An example of such an exception is illustrated in Fig. 1, where the experimentally obtained variation of H as a function of the weight fraction of the PE component, ϕ , (curve (3)) is plotted. It is seen that the H values for the initial PE and isotactic polypropylene (*i*PP) gel films ($H^{PE} = 105$ MPa and $H^{PP} = 116$ MPa) do not differ substantially from each other.

One can see a very clear deviation (straight line (1) of Fig. 1) with increasing PE concentration, ϕ , from the additivity law:

$$H = \phi H^{PE} + (1 - \phi) H^{PP} \quad (2)$$

Since the glass transition temperature of PE is much lower than the room temperature, the microhardness contribution of the amorphous phase has been accepted to be $H_a^{PE} \sim 0$ [10]. Hence, for PE, with a degree of crystallinity, w_c^{PE} , using the additivity model of Eq. (1) one may write:

$$H^{PE} = w_c^{PE} H_c^{PE} \quad (3)$$

On the other hand, since for *i*PP $H_a^{PP} \neq 0$, for *i*PP, with a degree of crystallinity, w_c^{PP} :

$$H^{PP} = w_c^{PP} H_c^{PP} + (1 - w_c^{PP}) H_a^{PP} \quad (4)$$

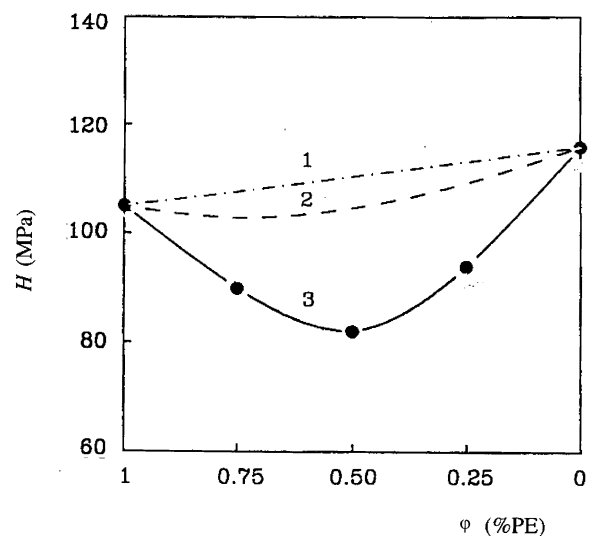


Fig. 1 Microhardness, H , of PE/*i*PP blended gel films as a function of PE concentration, ϕ : additivity behavior from Eq. (1) using the w_c values of the individual homopolymers (1); H values using w_c^{PE} and w_c^{PP} data (Table 1) (2); experimental data (3) [1, 10]

By combining Eqs. (3) and (4) one obtains for the overall microhardness of the blend, H , the expression:

$$H = \phi w_c^{\text{PE}} H_c^{\text{PE}} + (1 - \phi) w_c^{\text{PP}} H_c^{\text{PP}} + (1 - \phi)(1 - w_c^{\text{PP}}) H_a^{\text{PP}} \quad (5)$$

which describes the microhardness of the blended gel films in terms of the microhardnesses of the independent crystalline and amorphous components assuming $H_a^{\text{PE}} \sim 0$. If one takes into account the crystallinity depression measured for the PE and *i*PP components in Equation 5, use $H_c^{\text{PE}} = 130$ MPa and $H_c^{\text{PP}} = 145$ MPa, and let $H_a^{\text{PP}} = 90$ MPa [10] one obtains then curve (2) in Fig. 1 which is still far from the experimental values (Fig. 1, curve (3)).

It should be noted here that in the same paper [10] it is demonstrated that the differences between the experimentally measured and calculated H values disappear if the thermodynamically derived parameter b (accounting for the crystal surface free energy and the energy required to plastically deform the crystal [1]) is used for the calculations. However, it seems important to mention also that the values of the b parameter have been derived from the same H_{exp} values and later used for the calculation of the H values (Eq. (1)).

The same approach (assuming $H_a = 0$ for the soft component and/or phase) applied to thermoplastic elastomers of poly(ether ester) (PEE) type fails also to explain the large discrepancy (up to 100 MPa when the measured H values are in the range 20–40 MPa) between the experimental values and those calculated according to Eq. (1) [11, 12]. For this reason, one has to look for other factors, which may be responsible for such a discrepancy. Before discussing them let us recall briefly some of the characteristic features of the structure and morphology of thermoplastic elastomers of PEE-type, which illustrate in the best way the concept disclosed in the present study.

Thermoplastic elastomers of PEE type represent polyblock copolymers comprising poly(butylene terephthalate) (PBT) as the “hard” segments and poly(glycols) as “soft” segments, both of them forming “hard” and “soft” domains, respectively. Since the soft domains are characterized by T_g values around -50 °C, they are in a liquid state at room temperature and are distinguished by a viscosity being much closer to those of low-molecular-weight liquids rather than to that of a solid amorphous polymer. In this respect it seems useful to recall that the molecular weights of the poly(tetramethylene glycol) (PTMG) and poly(ethylene glycol) (PEG) used are around 1,000, i.e. one deals with typical oligomeric materials. For this reason, it

looks reasonable to accept that such a liquid (soft phase) will be characterized by a negligibly small microhardness, H^s , in the equation for the overall microhardness of such a copolymer, H :

$$H = \phi [w_c H_c^h + (1 - w_c) H_a^h] + (1 - \phi) H^s \quad (6)$$

where ϕ is the mass fraction of hard segments (PBT in the present case), H_c^h and H_a^h are the microhardnesses of the crystalline and amorphous phases of the same hard domains, respectively, and w_c is the degree of crystallinity of PBT.

Assuming, as in the case of the PE/*i*PP blend, the microhardness of the soft domains being $H^s = 0$, the calculations of H according to Eq. (1) for a series of PEEs lead to a discrepancy between the measured, H_{exp} , and calculated (using again Eq. (1)) H'_{cal} amounting to 40–64 MPa, depending on the soft-segment composition, as will be discussed below.

A question arises about the reason for the failure of the additivity law in the above-mentioned systems, both, the polyolefins blends [10] and the multiblockcopolymer. Obviously, one has to assume that, for multicomponent and/or multiphase systems, when one of the components (phases) is characterized by a viscosity at room temperature close to those of the low-molecular weight liquids, the mechanism of the response to the applied external mechanical field is different from that when all the components (phases) have T_g and T_m higher than room temperature. In the latter case all the components (phases) plastically deform as a result of the applied external force. In the former case, in addition to the plastic deformation of the harder components (phases), they are also displaced within the soft (liquid) matrix in which they are “floating”. The extent of this displacement depends on the viscosity of the matrix (the softer component and/or phase). This is the reason why the harder components cannot display their inherent microhardness. The microhardness is reduced by the ability of the harder components to move. This situation is illustrated in Fig. 2.

How can one account for this microhardness depression, i.e. for the “floating effect”? As demonstrated above, the simple assumption that the soft phases have $H^s \sim 0$, i.e. if one accounts only for its “diluting effect”, does not solve the problem. It is necessary to characterize the ability of the harder phase to move about within the soft matrix, and this will depend on the viscosity of the matrix, i.e. the soft phase. Since T_g and viscosity are closely related to each other, it is possible to look for an analytical relationship between microhardness of the amorphous polymers and their T_g .

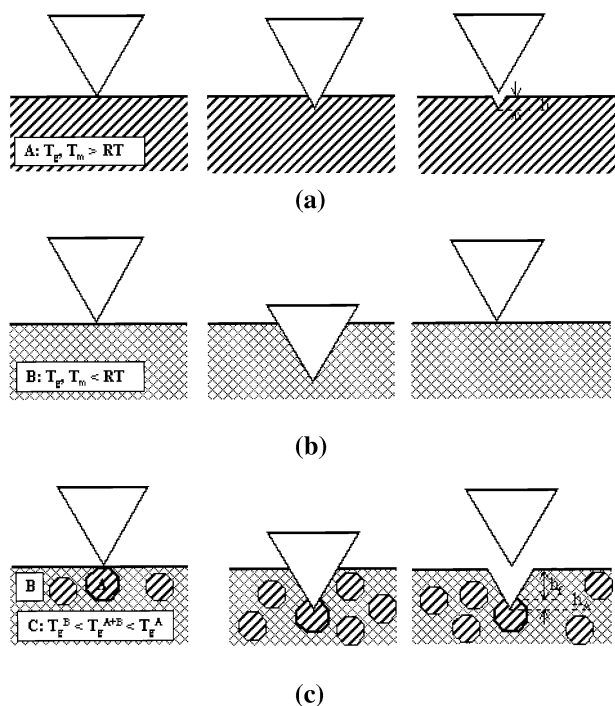


Fig. 2 Schematic the indentation mechanism for three types of samples: **(A)** With T_g and T_m above the test temperature (room temperature, RT), microhardness $H \approx 1/h$, **(a)**; **(B)** With T_g and T_m below RT, $H \approx 0$, **(b)**; **(C)** Complex system with matrix **B** and a “floating” dispersed phase **A**, $H \approx 1/(h_A + h_f)$, **(c)**. In all the cases the elastic recovery of the samples is not taken into account

The *main goal* of this study is, by means of larger number of studied systems, to show that the assumption $H^s = 0$ for the soft component and/or phase being dominating in complex polymer systems leads to drastic deviations from the additivity law (Eq. (1)). The contribution of the soft component and/or phase to the overall microhardness can be much more reliably accounted for using the relationship between T_g and the microhardness of the amorphous component and/or phase, particularly for systems characterized by dominating amorphous component and/or phase. A *secondary goal* of the work is to demonstrate, that the experimentally derived relationship between H and T_g can be applied for evaluation of the T_g value of a practically non-accessible component and/or phase.

Experimental

No experimental work was undertaken for this study since a good deal of data have already been reported in the literature in this respect. One needs only to evaluate the contribution of the soft component and/or phase through their glass transition temperature to the overall microhardness. Usually, samples differing in their crys-

tallinity are used, which are prepared by means of various techniques indicated to the respective system below. What deserves to be mentioned here is that in all the cases the microhardness measurements have been carried out at room temperature employing a Vickers pyramid diamond. The microhardness value, H , has been always derived from:

$$H = 1.854P/d^2 \quad (7)$$

where P is the applied load and d the diagonal of the residual impression. The permanent deformation has been measured immediately after load release to avoid long delayed recovery. Loads of a couple hundreds of mN have been used, for an indentation time of 0.1 min, in order to correct for the instant elastic recovery. This correction has been then applied to derive the H values using indentation times typically in the range 0.1–21 min and loads of around 150 mN.

Results

In accordance with the main goal of this study, i.e. recalculations of the overall microhardness by means of additivity law (Eq. (1)), however, assuming (in contrast to the approach used for the already published data), that the microhardness of the soft component and/or phase is not zero. Their contribution to the overall microhardness of the complex system is evaluated by means of the recently derived relationship between H and T_g for a series of amorphous homo- and copolymers [13]:

$$H = 1.97T_g - 571 \quad (H \text{ in MPa, } T_g \text{ in K}) \quad (8)$$

Subsequently, examples for comparison of the measured, H_{exp} , and calculated (with $H^s \neq 0$) microhardness values, H_{cal}'' will be considered below for two-component multiphase systems comprising soft phases (blends of polyolefins), multiblock copolymers of thermoplastic elastomers (TPE) of condensation type, blends of amorphous miscible polymers, blends of copolymers with different molecular architecture, and finally, homopolymers comprising amorphous phase with very low T_g (PE).

Two-component multiphase systems comprising soft phase(s) (blends of semicrystalline homopolymers)

The best studied system in this respect is the aforementioned blend PE/*i*PP [10]. As already commented (Fig. 1), a significant discrepancy between H_{exp} and

Table 1 Composition, crystallinity, w_c^{PE} , and w_c^{PP} , measured microhardness, H_{exp} , calculated microhardness (according to Eq. (1), with $H_a = 0$), H'_{cal} , and according to Equation 8, (with $H^s \neq$

0), H''_{cal} , and the differences between the measured and calculated values, $\Delta H'$ and $\Delta H''$, respectively, for PE/iPP blends

PE/iPP (by wt)	w_c^{PE} [10]	w_c^{PP} [10]	H_{exp} (MPa) [10]	H'_{cal} (MPa) (acc. Eq. (1)) [10]	$\Delta H' = H'_{cal} - H_{exp}$ (MPa)	H''_{cal} (MPa) (acc. Eq. (8))	$\Delta H'' = H''_{cal} - H_{exp}$ (MPa)
100/0	0.80	–	105	104	–1	–	–
75/25	0.77	0.39	90	108	18	72	–18
50/50	0.74	0.43	82	110	28	83	1
25/75	0.71	0.45	94	113	19	96	2
0/100		0.49	116	117	1	–	–

H'_{cal} (assuming $H_a^{PE} = 0$) can be observed (compare the values of H_{exp} with H'_{cal} in Table 1). If one tries to account for the contribution of the PE amorphous phase, (which amounts up to 30%), to the overall microhardness of the blend by means of its glass transition temperature T_g^{PE} using Eq. (8), for some of the samples, characterized by lower content in the blend (50 and 25 wt%) of the high crystalline PE (w_c between 70 and 80%), one obtains H''_{cal} values rather close to the measured ones (differences of 2–3%), as can be concluded from Table 1. For these calculations a value of $T_g^{PE} = -80$ °C is assumed being the most frequently used for the amorphous unbranched PE [14–19]. It is worth noticing here that much higher values for T_g of PE (around -30 °C) are also reported [20–25], however, they are derived from branched PE [20–24] or samples characterized by highly strained amorphous chains [25].

Basically, the unsatisfactory agreement between H'_{cal} (assuming $H^s \neq 0$) and H_{exp} for the blend with the highest content of PE (75 wt%) could have another, additional origin. In order to apply Eq. (8) correctly, one needs to know the T_g values of the amorphous phase of the particular sample under investigation. This was not the case for the discussed system PE/iPP for which the common value of $T_g = -80$ °C was used, although the real value can be higher, particularly in the cases with high degree of crystallinity. What is more, a higher T_g value would lead to a smaller difference $\Delta H''$ for the same sample. Therefore, for the next systems only the experimentally measured T_g values of the respective soft component and/or phase will be used for the similar calculations.

One-component multiphase systems containing soft phase(s) (polyblock copolymers)

Micromechanical studies have also been carried out on thermoplastic elastomers. The latter represents a special class of multiphase systems (block copolymers) exhibiting an unusual combination of properties: they

are elastic and at the same time tough and they show low-temperature flexibility and also strength at relatively high temperatures (frequently ca. 150 °C) [26, 27].

In addition to the thermoplastic elastomers of PEE type, also a series of new poly(ester ether carbonate) (PEEC) multiblock terpolymers with varying amount of ether and carbonate soft-segment content will be considered. Dielectric relaxation experiments on the same PEEC revealed the existence of two relaxation processes [28]. The dielectric loss values show a relaxation maximum appearing at about 0 °C for 10 kHz (β relaxation) accompanied by a lower temperature relaxation (γ relaxation) that appears at about -50 °C.

The microhardness of films of thermoplastic elastomers based on PBT–cycloaliphatic carbonate (PBT–PCc) block copolymers has also been studied [29]. The microhardness of their amorphous films has been discussed in terms of a model given by the additivity values of the single components H_a^{PBT} and H_a^{PCc} . In the case of semicrystalline copolymers, the authors related the observed deviation from the additivity law as mainly due to the depression of the crystal microhardness of the PBT crystals and partly due to a decrease in crystallinity of the PBT phase [29]. The measured H values for the terpolymers studied [29] are very low in comparison to the values known for common synthetic polymers even those in the amorphous state [30]. What is more, the H_{exp} values are more than three times smaller than the calculated ones. For the purpose of such calculations, the authors [29] present the additivity law (Eq. (1)) in the following form:

$$H = \phi H^{PBT} + (1 - \phi) H^s \tag{9}$$

where ϕ is the weight fraction of the hard PBT segments and H^s the microhardness of the soft domains. Further, taking into account the fact that the T_g of the soft-segment amorphous phase lies between -50 and 0 °C, (depending on the PCc

Table 2 Composition, degree of crystallinity of PBT, w_c , glass transition temperatures of the soft, T_g^s , and the hard, T_g^h , domains, measured microhardness, H_{exp} , calculated microhardness (according to Eq. (1) with $H^s = 0$), H'_{cal} , and according to

Eq. (8) (with $H^s \neq 0$), H''_{cal} , and the differences between measured and calculated values, $\Delta H'$, and $\Delta H''$, for PEEC block terpolymers

PBT/PTMG/ PCc (by wt)	w_c (%) [29]	T_g (°C) [29]			Microhardness (MPa)				
		T_g^s from DSC	T_g^s from DMTA	T_g^h from DSC	H_{exp} [29]	H'_{cal} [29]	$\Delta H' = H'_{cal} - H_{exp}$	H''_{cal}	$\Delta H'' = H''_{cal} - H_{exp}$
100/0/0	59.0	55	–	–	–	–	–	–	–
60/40/0	37.7	–56	–50	57	29.6	85.1	55.5	28	–1.6
60/32/8	25.8	–45	–34	55	22.8	68.5	45.7	20	–2.8
60/20/20	24.3	–32	–17	54	18.6	66.4	47.8	28	9.4
60/12/28	21.2	–10	–3	53	17.5	62.0	44.5	41	23.5
60/0/40	13.0	1	19	52	15.5	50.6	35.1	38	22.5

content [29]), the authors assumed again that $H^s \sim 0$. As a result, H will be depressed with decreasing values of ϕ according to the simple expression [29]:

$$H = \phi H^{PBT} = \phi [w_c H_c^{PBT} + (1 - w_c) H_a^{PBT}] \quad (10)$$

Again, in this case also the assumption $H^s = 0$ means to take into account only the “diluting effect” of the soft phase and no attempt to be made for considering the possibility for another deformation mechanism. So, by applying the numerical values $\phi = 0.6$, $H_c^{PBT} = 287$ MPa, and $H_a^{PBT} = 54$ MPa [29] one can derive the calculated values H'_{cal} for the terpolymers depending on their crystallinity w_c (Table 2).

The differences between H_{exp} and H'_{cal} are quite obvious—the calculated values are two to three times higher than the measured ones (Table 2).

For a quantitative evaluation of the microhardness depression effect of the soft phase, one has to replace H^s in Eq. (9) with Eq. (8) using for T_g the experimentally measured values of the soft-segment phase T_g^s . This leads to the expression:

$$H = \phi [w_c H_c^h + (1 - w_c) H_a^h] + (1 - \phi)(1.977 T_g^s - 571) \quad (11)$$

Calculation of H for PEE and PEEC by means of Eq. (11) offers data that are in a very good agreement with the measured H_{exp} values as shown in Table 2 for PEEC and Table 3 for PEE and PEEC (samples 1–6).

Another system of interest demonstrating the limits of the additivity law (Eq. (1)) (with the assumption $H^s = 0$) is again a thermoplastic elastomer of novel type—multiblock polyester-amide copolymers, synthesized recently [31]. These materials, similarly to PEE, possess a hetero-phase structure, with two T_g values and only one melting temperature above room temperature, which corresponds to the fusion of PBT crystals. The diamide segments are chosen to mainly contribute to the amorphous domains and confer to the material an elastomeric character.

Data on the molecular weight of the used oligotetrahydrofuran, blocks fractions (in mol%), temperature transitions, degree of crystallinity, and

Table 3 Composition, annealing temperature (T) of $5 \times$ drawn samples, degree of crystallinity of PBT, w_c , glass transition temperature of the soft domains, T_g^s , measured microhardness, H_{exp} , calculated microhardness, H'_{cal} , (according to Eq. (1), with

$H^s = 0$) and H''_{cal} (according to Eq. (8), with $H^s \neq 0$), and the difference between measured and calculated values, $\Delta H'$ and $\Delta H''$, respectively, for thermoplastic elastomers of PEE- or PEEC-type [1]

Copolymer	Composition (by wt)	T (°C)	w_c (%) [1]	T_g^s (°C) [1]	Microhardness (MPa)				
					H_{exp} [1]	H'_{cal} (acc. Eq. (1)) [1]	$\Delta H' = H'_{cal} - H_{exp}$	H''_{cal} acc. Eq. (11)	$\Delta H'' = H''_{cal} - H_{exp}$
PBT/PTMG	60/40	70	37.7	–56	29.6	87.5	56.1	29.7	0.1
PBT/PTMG/ PCc	60/32/8	70	25.8	–45	22.8	69.5	46.7	21.8	1.0
PBT/PTMG/ PCc	60/20/20	70	24.3	–32	18.68	59.9	41.3	22.0	3.4
PBT/PEG	57/43	170	41	–44.5	34.2	85.2	51	34.4	0.2
PBT/PEG	57/43	25	37	–37	30.7	79.9	49.2	31.6	0.9
PBT/PEG	57/43	170	41	–41	32.9	85.2	52.3	35.4	2.3
PBT/PEG	75/25	25	35	–35	47.3	101.7	54.4	85.1	37.8
PBT/PEG	75/25	150	39	–39	44.2	108.5	64.3	83.7	39.5

density, together with the measured and calculated H_{exp} and H'_{cal} (with $H^s = 0$) values are reported [32]. Hardness is shown to drastically decrease with increasing etherdiamide content. The experimentally measured hardness values of the copolymers clearly deviate from the linear additivity law, where the authors [32] assume $H^s \sim 0$ for the poly(etherdiamide) homopolymer, as its T_g is far below the room temperature. Following the same logic as in the case of PEE, PEEC and PE, they have used the following equation, which formally describes the hardness of a two-component system in terms of the H values of the individual constituents [32]:

$$H = (1 - \phi^{DA})H^{PBT} + \phi^{DA}H^{DA} \tag{12}$$

Here, H^{PBT} and H^{DA} are the microhardness values of the PBT and etherdiamide domains, respectively, ($H^{DA} \sim 0$) and ϕ^{DA} is, in this particular case, the mole fraction of the soft segments (etherdiamide component). In analogy with the previous cases, the value of H^{PBT} has been expressed in terms of the crystal hardness, H_c^{PBT} , the hardness of the PBT amorphous regions, H_a^{PBT} , and as a function of the volume degree of crystallinity of PBT referred to the volume fraction of PBT “component” in the sample, v_c^{PBT} . Therefore, one can rewrite Eq. (12) to yield [32]:

$$H = (1 - \phi^{DA})[v_c^{PBT}H_c^{PBT} + (1 - v_c^{PBT})H_a^{PBT}] \tag{13}$$

Using the volume fraction crystallinity, $v_c = v_c^{PBT} (1 - \phi^{DA})$, Eq. (13) finally reads [32]:

$$H = v_c^{PBT}H_c^{PBT} + (1 - v_c^{PBT} - \phi^{DA})H_a^{PBT} \tag{14}$$

H_a^{PBT} has been reported to be of 54 MPa [29, 33]. It has been found [32] that the calculated by means of Eq. (14) values H'_{cal} , i.e. assuming again $H^s = 0$, are 8–10 time larger than the measured H_{exp} values for the two-third of the samples under investigation. For this reason, one has to look again for another reason for the observed discrepancy. In order to apply again the “floating effect” concept, one has to replace in Eq. (12) the H^{DA} with $H^{DA} = 1.97T_g^{DA} - 571$ and combining further with Equation 13 to obtain for the overall microhardness:

$$H = (1 - \phi^{DA})[w_c^{PBT}H_c^{PBT} + (1 - w_c^{PBT})H_a^{PBT}] + \phi^{DA}(1.97T_g^{DA} - 571) \tag{15}$$

where w_c is the weight fraction crystallinity of PBT.

The calculated values for H'_{cal} according to Eq. (15) also differ from the measured one, and what is more, they are not consistent—only one third of them show small differences (around 3–8%) from the H_{exp} values, while the rest scatter in a large interval contrasting the results from the thermoplastic elastomers of PEE type (Tables 2 and 3). An attempt to explain these differences will be undertaken later, when discussing the obtained results.

Two-component one-phase systems (miscible blends of amorphous polymers)

In addition to the studies on blends of polyolefins, as well as on multiblock copolymers described above, in which some of the components and/or phases are crystallizable, investigations have also been carried out on blends of non-crystallizable components.

Amorphous films of poly(methylmethacrylate)/poly(vinylidene fluoride) (PMMA/PVDF) blends have been prepared by initial precipitation from a solvent and rapid solidification at $\sim 15^\circ\text{C}$ from the molten state [34]. Moreover, these two constituents are considered as miscible [35, 36]. The PMMA/PVDF compositions studied have 25/75, 45/55, 50/50, 55/45, 60/40 and 75/25 ratios (by weight). The presence of a single X-ray halo as well as a single T_g value for all the blends, in the above composition range, favored the view that these materials are composed of homogeneous mixtures at molecular level [34]. For this reason, the authors assumed [34] that the parallel decrease of the microhardness obeys a simple expression for the overall microhardness of the blend, H :

$$H = H^{PMMA}(1 - \phi^{PVDF}) \tag{16}$$

where ϕ^{PVDF} is the mass fraction of PVDF. Since the T_g value of PVDF is known to be -40°C [35], the authors have applied the common approach to that time, assuming that the PVDF molecules do not offer any mechanical contribution to the yield behavior of the blend [34].

If one follows this logic and calculates the H values from Eq. (16) taking into account only H_a^{PMMA} value and PMMA mass fraction, one obtains values being quite different from the experimental ones, as can be concluded from Table 4, where the measured values of T_g and of the density for the blends are given, as reported in [34].

If one applies the other approach for accounting the contribution of the soft component, as in the two cases described in the previous sections, i.e. via the T_g value,

the results look quite differently, as demonstrated below.

Formally, the blend PMMA/PVDF can be considered as a three-phase one, because the reported density, ρ , values (Table 4, [34]) differ from the commonly accepted for ρ_a one. For the neat PVDF a density value of $1,740 \text{ kg m}^{-3}$ is reported [34] while in the literature a value for the fully amorphous PVDF (ρ_a) of $1,680 \text{ kg m}^{-3}$ can be found [14, 36]. This difference in ρ_a suggests that some “ordering” in the system may have taken place during the sample preparation. Using the value of $\rho_c = 1,930 \text{ kg m}^{-3}$ for the completely crystalline PVDF [36] (which corresponds to the α -, also called type I-modification, i.e. crystallization from melt), one could estimate an apparent “degree of crystallinity” $w_c = \rho_c / \rho [(\rho - \rho_a) / (\rho_c - \rho_a)]$ for the sample with $\rho = 1,740 \text{ kg m}^{-3}$, leading to $w_c = 0.25$.

Based on the fact that all the samples (Table 4) have been prepared in the same manner [34], 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 4) as two-phase systems, In case of such blends the microhardness can be calculated by means of the additivity law as:

$$H = \phi[w_c H_c^{\text{PVDF}} + (1 - w_c) H_a^{\text{PVDF}}] + (1 - \phi) H_a^{\text{PMMA}} \tag{17}$$

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 Eqs. (17) and (8) one obtains [37]:

$$H = \phi[w_c H_c^{\text{PVDF}} + (1 - w_c)(1.97 T_g^{\text{PVDF}} - 571)] + (1 - \phi)(1.97 T_g^{\text{PMMA}} - 571) \tag{18}$$

H_c^{PVDF} can be easily evaluated using the extrapolated microhardness value for the neat PVDF (with $w_c = 25\%$) of $H = 0 \text{ MPa}$ and the value of $H_c^{\text{PVDF}} = 336 \text{ MPa}$ is obtained. Using this value of H_c^{PVDF} and letting $T_g^{\text{PVDF}} = 233 \text{ K}$ and $T_g^{\text{PMMA}} = 393 \text{ K}$ (Table 4), one can calculate by means of Eq. (18) the microhardness of the studied blends. The values obtained are summarized in Table 4 as H''_{cal} from Eq. (18).

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

Table 4 Composition of PMMA/PVDF blends, their glass transition temperatures, T_g^B , density, ρ , the experimentally measured microhardness, values, H_{exp} , calculated by means of Eq. (1) (with $H^s = 0$), H'_{cal} , or calculated with $H^s \neq 0$ values, H''_{cal} , as well as the differences between the calculated and the measured values, $\Delta H'$, $\Delta H''$ and $\Delta H'''$, respectively

PMMA/ PVDF (by wt)	T_g^{exp} (K) [34]	T_g^{B} (K) [37]	ρ (kg m^{-3}) [34]	H_{exp} (MPa) [34]	H'_{cal} (MPa) (Eq. (1))	$\Delta H' = H'_{\text{cal}} - H_{\text{exp}}$ (MPa)	H'_{cal} (MPa) (Eq. (8))	$\Delta H'' = H''_{\text{cal}} - H_{\text{exp}}$ (MPa)	H''_{cal} (MPa) (Eq. 19)	$\Delta H''' = H'''_{\text{cal}} - H_{\text{exp}}$ (MPa)
100/0	393	-	1,183	212	201	-11	203	-9	203	-9
75/25	359	336	1,276	160	91	-69	152	-8	106 (148)	-54 (-12)
55/45	337	340	1,370	125	100	-25	117	-12	125	0
50/50	331	333	1,390	107	84	-32	102	-5	113	6
45/55	325	325	1,419	103	69	-34	92	-11	106	3
40/60	319	317	1,444	70	53	-17	81	11	93	13
25/75	293	291	1,546	53	23	-50	52	-1	65	12
0/100	233	-	1,740	0 (extr.)	-112	-112	1	1	0	0

The suggested treatment (Eq. (17)) considers formally the PMMA/PVDF blends as a three-phase system—two amorphous and one “crystalline” (PVDF). Now, let try to calculate the H 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 , that of the blend, T_g^B . Then H will be [37]:

$$H = \phi_c H_c^{PVDF} + (1 - \phi_c)(1.97T_g^B - 571) \quad (19)$$

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

Using the values for T_g^B as derived from Gordon and Taylor equation [38] one obtains by means of Eq. (19), the values of H listed also in Table 4 on its last column as H_{cal}''' . A relatively good agreement with the reported [34] H_{exp} values can be observed (Table 4). In specific cases the agreement is even better than in the previous three-phase model treatment (according to Eq. (17)).

The most serious exception in this respect is the blend 75/25, for which much better value (see the value in parentheses, Table 4) is obtained if one uses the measured $T_g^B = 359$ K (Table 4) instead of the calculated by means of Gordon and Taylor equation 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 [39, 40].

Two-component two-phase amorphous systems containing a soft phase

In recent publications on blends of novel copolymers of polystyrene (PS) with polybutadiene (PB), with well-defined linear block- or star block architecture, detailed morphological and mechanical investigations have been performed [41–43]. Studying the microhardness behavior of these copolymer blends, the authors, in analogy with previous cases discussed above, have drawn the following conclusion regarding the contribution of the soft phase to the overall microhardness: “since the T_g of the phase in the present case is always well below the test temperature (i.e., the room temperature, 23 °C), which may be regarded as being at liquid-like state, it does not affect the measured H values. Therefore, there is no correlation between the soft phase glass transition temperature and the microhardness of the polymer blends discussed in the present study” [41].

At the same time, for the blends of the star block and a linear triblock copolymers, both consisting of PS and PB, has been found that the experimental hardness of the blends show much lower H values than those predicted from the additivity law (again assuming $H^s = 0$), as shown in Fig. 3. This finding is similar to the results obtained for microphase separated blends styrene/butadiene block copolymers [42].

To what extent the cited assumption of the authors [41] regarding the lack of influence of the liquid-like phase on the H values is correct and if the observed deviation from the additivity law is not due to the neglecting of this influence?

For the studied two-component system [41] consisting of two copolymers (linear and star-like) based on the same two monomers (styrene and butadiene) the additivity law (Eq. (1)) can be presented in the following way, accounting also for the contribution of the soft phases to the overall microhardness, H :

$$H = \phi_{block} [w_{PS} H^{PS} + (1 - w_{PS}) H^{PB}] + (1 - \phi_{block}) [w'_{PS} H^{PS} + (1 - w'_{PS}) H^{PB}] \quad (20)$$

where H^{PS} and H^{PB} are the microhardness of the respective homopolymers, w_{PS} , w'_{PS} and $(1 - w_{PS})$, $(1 - w'_{PS})$, are mass fractions of PS and PB in each copolymer, respectively, and ϕ_{block} and $(1 - \phi_{block})$ are the mass fraction of the copolymers in the blend. Taking into account the important fact that the two copolymers (as well as their blocks) are completely amorphous, one can express their microhardness by

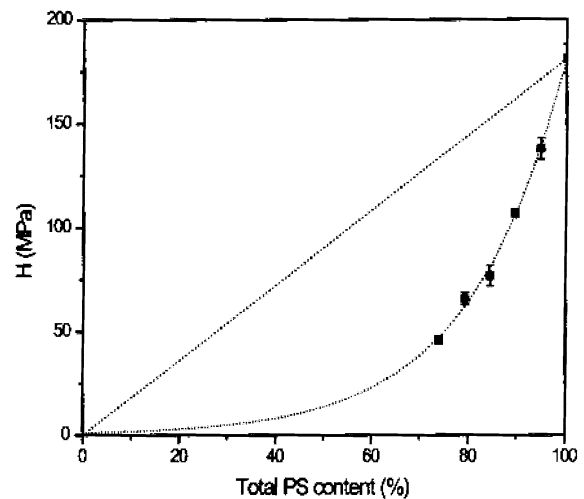


Fig. 3 Microhardness of the blend of linear and star-like copolymers of PS and PB, H , as a function of the total PS content (assuming volume fraction \approx weight fraction), ϕ_{PB} ; dashed straight line represents the additivity law (Eq. (1)) [41]

means of Eq. (8) and obtain for the overall H of the blend the following expression:

$$H = \phi_{\text{block}} [w_{\text{PS}}(1.97T_{\text{g}}^{\text{PS}} - 571) + (1 - w_{\text{PS}})(1.97T_{\text{g}}^{\text{PB}} - 571)] + (1 - \phi_{\text{block}}) [w'_{\text{PS}}(1.97T_{\text{g}}^{\text{PS}} - 571) + (1 - w'_{\text{PS}})(1.97T_{\text{g}}^{\text{PB}} - 571)] \tag{21}$$

Equation (21) reflects analytically the contribution to the overall microhardness H of each constituent of the blends (copolymers and their blocks). At the same time, one should not forget a very important fact—experimentally are observed only two glass transition temperatures (that of PS and that of PB), regardless of the fact that blocks of them are incorporated in the two type of copolymers [41]. For this reason, it seems justified to use for the calculation of the overall microhardness of the copolymer blend H (assuming again $H^s \neq 0$) a more simple equation accounting only for the total mass fraction in the blend of the two species, PS and PB, and their T_{g} values:

$$H = \phi_{\text{PS}}(1.97T_{\text{g}}^{\text{PS}} - 571) + (1 - \phi_{\text{PS}})(1.97T_{\text{g}}^{\text{PB}} - 571) \tag{22}$$

where ϕ_{PS} and $(1 - \phi_{\text{PS}})$ are the total mass fractions in the blends of PS and PB, respectively.

Using the reported data [41] about the total mass fractions of PS and PB in the blends (ϕ_{PS} and $(1 - \phi_{\text{PS}})$, respectively), and the values of T_{g} for both type of phases (as summarized in Table 5), one can calculate the respective H values, H''_{cal} , of the studied blends by means of Eq. (22), and compare them with the experimentally measured ones, H_{exp} , as well as with the calculated values using Eq. (1) and assuming $H^s = 0$, H'_{cal} , (given also in Table 5).

One can see that the difference between the measured H values and the calculated ones, however neglecting the contribution of the soft phase ($H^s = 0$, i.e. using a relationship similar to Eq. (16)), is quite large (H_{exp} values are between 2 and 5 time smaller than those of H'_{cal}). Even so, when accounting for the contribution of the soft phase ($H^s \neq 0$, i.e. by means of Eq. (22)), the two types of values are much closer to each other (Table 5).

What is more, since the system under investigation is completely amorphous, it is possible to predict its microhardness for various compositions having only the T_{g} and weight fraction of each phase, as described in Eq. (21). The good agreement between calculated

Table 5 Content of the linear block copolymer, LN4, in the copolymer blends, total polybutadiene content, ϕ_{PB} , (assuming volume fraction \sim weight fraction), glass transition temperatures of PS, T_{g}^{PS} , and of PB, T_{g}^{PB} , phases, measured microhardness of the blend, H_{exp} , calculated microhardness (according to Eq. (1), with $H^s = 0$), H'_{cal} , and according to Equation 8 (with $H^s \neq 0$), H''_{cal} , as well as the differences between the measured and the calculated values, $\Delta H'$ and $\Delta H''$, respectively

LN4 content (wt%)	ϕ_{PB} (%) [41]	T_{g}^{PS} (°C) [41]	T_{g}^{PB} (°C) [41]	T_{g}^{PB} (°C) [41]	T_{g}^{PB} (°C) [41]	H_{exp} (MPa) [41]	H'_{cal} (MPa) Eq. (1)	H'_{cal} (MPa) [41]	$\Delta H' = H'_{\text{cal}} - H_{\text{exp}}$ (MPa)	H''_{cal} (MPa) Eq. (8)	$\Delta H'' = H''_{\text{cal}} - H_{\text{exp}}$ (MPa)
0	26	104	-74	-	44	130	86	78	34		
20	34	104	-68	-64	28	116	88	56	28		
40	42	103	-53	-54	24	102	78	40	16		
60	49	100	-31	-43	16	89	73	37	21		
80	57	87	-25	-30	12	75	63	12	0		
100	65	70	-15	-	8	61	53	-4	4		

and the measured H values demonstrate again the validity of the analytical relationship between H and T_g (Eq. (8)).

Quite similar is the situation regarding the microhardness behavior of binary blend comprising the polystyrene homopolymer (hPS) and a star block copolymer of styrene with butadiene over a wide composition range. As in the case of separated block copolymers and binary block copolymer blend, as described above [41, 42], a clear deviation of the microhardness behavior from the additivity law has been also observed [43].

Using an equation similar to the last one (Eq. (22)), however, accounting for the fact that one of components of the blends is a homopolymer and applying the respective values for T_g , and mass fractions ([43], Table 6), the H values of the blends are calculated assuming that $H^s \neq 0$. The results are presented in Table 6.

Again a much better agreement between H_{exp} and H'_{cal} values is found if one accounts for the contribution of the soft phase ($H^s \neq 0$), in contrast to the opposite case ($H^s = 0$), (Table 6), however, the differences $\Delta H''$ are still quite large, as compared with the case of PEE (Tables 2 and 3).

One-component two-phase systems (semicrystalline polymers with T_g below room temperature)

As demonstrated above, there is hardly any doubt regarding existence of a linear relationship between T_g and the microhardness H of the amorphous polymers characterized by dominating single, mostly C–C bonds in the main chain. This empirically derived analytical relationship (Eq. (8)) makes it possible to account quantitatively for the contribution of the soft component and/or phase to the overall microhardness of multicomponent and/or multiphase systems as demonstrated above.

The same relationship offers another challenging opportunity—to evaluate the T_g of amorphous phase(s), which are not commonly accessible, as for example, the wholly amorphous PE. Basically, this can be done starting again from the additivity law, and more specifically, by the fact that the overall microhardness depends linearly on those of its constituent components and/or phases and their respective weight fractions. For a semicrystalline polymer one can extrapolate the dependence H_c versus degree of crystallinity, w_c , (or density) to $w_c = 0$ (or to the ρ_a value) and thus evaluate H_a for this polymer. Further, exploring the relationship between H and T_g (Eq. (8)) it is possible to get an idea about T_g of an inaccessible practically amorphous phase. This approach will be illustrated below using as example PE.

Polyethylene 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 [14]. These discrepancies can be found also in more recent publications: $T_g = -35$ °C [44], and $T_g = -125$ °C [45]. The lack of agreement is related to the fact that PE is not commonly accessible in 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 capable to prepare a series of samples with a systematic variation

Table 6 Content of the homo PS in the blends, hPS, total polystyrene content in the blends, ϕ_{PS} , (assuming volume fraction \sim weight fraction), measured microhardness of the blends, H_{exp} , calculated microhardness (according to Eq. (1),

with $H^s = 0$), H'_{cal} , and according to Equation 8 (with $H^s \neq 0$), H''_{cal} , as well as the differences between the measured and the calculated values, $\Delta H'$ and $\Delta H''$, respectively

hPS content (wt%)	ϕ_{PS} (wt%)	H_{exp} (MPa) [42]	H'_{cal} (MPa) [42] (acc. Eq. (1))	$\Delta H' = H'_{cal} - H_{exp}$ (MPa)	H''_{cal} (MPa) (acc. Eq. (8))	$\Delta H'' = H''_{cal} - H_{exp}$ (MPa)
0	74	44	127	83	81	37
20	79	64	136	72	98	34
40	84	75	144	70	115	40
60	90	100	155	55	137	37
80	95	138	163	25	154	16
100	100	180	172	8	–	–

in the structural parameters such as degree of crystallinity, crystal size, long spacing, density, paracrystalline lattice distortions, melting temperature, etc. [46–48]. Following a given property of such a series and extrapolating to the density of completely amorphous sample, one can find support in favor of one of the two rather different values of T_g for PE.

It has been found that H increases linearly with the rise of crystallinity, as reported for many polymers [1, 9]. From the straight line of the plot of H versus density, ρ , for differently branched PE samples, the H value for the completely amorphous PE ($\rho = 855 \text{ kg m}^{-3}$ [14]) has been evaluated [49]. The obtained H value has been further used for the evaluation of T_g of PE by means of the linear relationship between H and T_g for completely amorphous polymers (Eq. (8)), and a value of $T_g = -23 \text{ }^\circ\text{C}$ has been obtained [50].

Taking into account the findings of Geil et al. [15–19] based on the direct study of wholly amorphous linear PE, that the T_g of PE is $-80 \text{ }^\circ\text{C}$ from one hand, and from the other, that branched PE is supposed to have a much higher T_g value (corresponding to the β -relaxation peak), one can consider the extrapolated T_g value of $-23 \text{ }^\circ\text{C}$ from branched PE samples as the T_g of completely amorphous branched PE [50].

Noteworthy in this respect is also the report of Perena et al. [20] who studied microhardness using dynamic mechanical (DMTA) measurements at low temperatures (between -60 and $25 \text{ }^\circ\text{C}$) with five commercial samples PE, two of them of HD and another three of low density (LD). The experimental data for H show clear transition around $-30 \text{ }^\circ\text{C}$ (for LD samples) and around $-10 \text{ }^\circ\text{C}$ (for HD) samples). The data from DMTA show this transition only for the LD samples in agreement with the observation [21] that β -relaxation is clearly detected by DMTA only in branched PE and has been not detected at all in linear PE of medium molecular weight. Having in mind the fact that the PE used for the application of Eq. (8) is also branched one, it should be emphasized that there is very good agreement between the experimentally observed transition temperatures (between -20 and $-30 \text{ }^\circ\text{C}$) [20] and those predicted by means of Eq. (8) (-23 and $-25 \text{ }^\circ\text{C}$) [24].

The same approach was very recently applied to PE samples characterized by chain-folded and chain-extended crystals [25]. Considering the fact that in these samples the amorphous phase amounts low percentage (in the chain-extended samples around 5 wt%) and because of the highly strained chains in the amorphous areas, one can expect relatively high values for T_g of these amorphous phases. The calculations

lead to $T_g = -1 \text{ }^\circ\text{C}$ (for the chain-folded samples) and $T_g = 10 \text{ }^\circ\text{C}$ (for the chain-extended samples) [25].

Summarizing this section, we have to note that thanks to the empirical linear relationship between H and T_g in a rather broad range of T_g ($-50 \text{ }^\circ\text{C}$ up to $250 \text{ }^\circ\text{C}$), which covers most commonly used polymers of the polyolefin type and also polyesters and polyamides [13], it is possible to calculate not only the microhardness value of many amorphous polymer provided its T_g is known ($H = 1.97T_g - 571$) or to account for the contribution of soft components and/or phases to the microhardness of the entire system, but also, to evaluate the T_g values of practically inaccessible amorphous phases in semicrystalline polymers.

Discussion

Importance of the ratio hard/soft components (or phases)

Analyzing the results summarized in Table 1 one can conclude that the agreement between the H_{exp} values and the calculated H_{cal} ones (assuming $H_a \neq 0$) is not as good as expected for all the samples. Quite close to each other are the values for the samples characterized by lower w_c values (below 80%) and higher amount of PP in the blends. This could mean that for the cases where the crystalline phase (or component) dominates (80% or more) the overall microhardness is determined by the “diluting effect” of the amorphous phase, i.e. the amount of the amorphous phase is not enough in order to be considered as a matrix in which the crystallites are immersed. As a matter of fact, in such cases the matrix is represented by the crystalline phase in which is dispersed the much smaller in amount (30% or less) amorphous phase. It is quite obvious that in such a situation one cannot apply the concept of the “floating effect” for explanation of the mechanical behavior of the complex system and one has to accept the plastic deformation mechanism of the solid component and/or phase as dominating.

The above considerations are supported by the results of the thermoplastic elastomers (PEE) with various compositions (hard/soft segments ratio). For example, in Table 3 data for other two PEEs (samples 7 and 8) with not such a good agreement between H_{exp} and H_{cal} (according to Eq. (11)) values are presented. A possible explanation for the different behavior of these two PEE samples is their composition. Samples 1–6 are characterized by hard/soft segments ratios of

roughly 60/40 while in the samples 7 and 8 this ratio is 75/25. The fact that in the second case the hard PBT segments dominate, suggests another response mechanism to the mechanical field—the PBT hard segments are no longer “floating” in the liquid-like matrix of soft domains.

Further support in favor of the importance of the hard/soft components ratio can be found in the blend hPS/star block copolymers of PS and PB (Table 6). A more precise inspection of Table 6 shows that the total amount hard, glassy homopolymer PS in the blends varies between 75 and 95 wt%. In other words, we are coming to the same conclusion as for the above two systems (PE/iPP and PEE), where for the cases when the hard, (crystalline) phase dominates (for example, amounting 80% and more) the concept of “floating effect” cannot be applied as successfully as for the cases when the hard component or phase does not dominate.

Crystalline or amorphous solids

In order to illustrate to what extent the presence or absence of order (crystalline) in the hard component and/or phase is important, let us come back first to the system polyester-polyamide copolymers for which serious deviations from the additivity law (assuming $H^s = 0$) have been reported [32]. Before suggesting some possible reasons for the failure of the calculations using Eq. (15) (assuming $H^s \neq 0$), one has to stress the fact that the paper under consideration [32] is distinguished by a couple of peculiarities being rather important for this discussion.

In this study [32] a relatively large number of interesting samples, differing in their hard/soft segments ratio as well as in the molecular weight of the segments, is investigated. The measured H_{exp} values differ drastically from the H'_{cal} values (assuming $H^s = 0$), the difference being up to ten times (while 9 from totally 12 samples have H_{exp} values between 10 and 30 MPa, the H'_{cal} for all the samples vary between 70 and 110 MPa). What is more striking, is the fact that the degree of crystallinity of PBT domains w_c (determined by wide-angle X-ray scattering, WAXS) for all the samples studied varies between 10 and 30% (for 9 of the samples—between 10 and 20%). Nevertheless, the drastic differences between H_{exp} and H'_{cal} values (assuming $H^s = 0$) are explained exclusively on the basis of the changes in the crystal's characteristics as crystal sizes, crystal surface free energy, the energy needed for plastic deformation of crystals (usually approximated to the enthalpy of fusion of crystals [1, 32]).

At this stage important questions could arise: how it would be possible to explain (or even to predict) the mechanical behavior of a complex system consisting of 80 wt% (and more) soft, liquid-like (T_g between -40 and -70 °C) matrix in which are dispersed not more than 20 wt% crystallites only accounting for the properties of crystallites? Does it look reasonable to neglect the contribution of the prevailing (up to 5 time) soft phase in the formation of the mechanical response of the system to the external load?

The samples studied [32] represent an excellent example for the case when the solid particles (crystallites in this case) are “floating” in the dominating soft matrix. As noted above, our attempt to recalculate the H''_{cal} values taking into account the “floating effect” ($H^s \neq 0$) failed. The data obtained are inconsistent, possibly because, for the fraction of the soft segments the molar concentration has been used [32].

It should be noted that there are not obvious reasons, except the misleading fact that the soft liquid-like substances do not produce Vickers indentation impressions, to accept that the soft component and/or phase does not contribute to the overall microhardness, i.e. $H^s = 0$. Only taking into account the fact that the soft component changes dramatically the deformation mechanism of the complex system, one is able to avoid more “sophisticated” explanations for the observed discrepancies between the H_{exp} and H_{cal} values (assuming $H^s = 0$). For example, in the case of the blends of PS and PB copolymers, as well as with various partners, these differences are explained by different origins: the molecular architecture which modifies the effective phase ratio, the presence of a microphase separated morphology and some specific effects such as yielding of thin layers, etc. [43] or by the assumption that the volume fraction of styrene and butadiene phases in the block copolymer blends does not reflect the effective hard/soft phase volume ratio owing to the modified copolymer architecture and microphase separated morphologies [41].

Quite similar explanations of the observed deviations from the additivity law dealing with semicrystalline polymers and their blends involving peculiarity in the crystalline characteristics (crystal sizes, crystal surface free energy, etc.) are offered, as mentioned in the previous sections. The most serious drawback of such explanations, even if they indicate on some of the possible reasons for the observed deviations from the additivity law (Eq. (1)), is that they cannot account quantitatively for the observed differences as, for example, Eq. (8) does.

Let consider now the blend of homo PS with star block copolymer of PS and PB, where the agreement

between the values of H_{exp} and H''_{cal} (even assuming $H^s \neq 0$) was not as good as expected (Table 6).

It seems important to stress here on a peculiarity of this system, namely, its similarity with the blend PE/*i*PP, with respect to their microhardness behavior. Regardless of the seemingly important facts that the blends of hPS with copolymers are completely amorphous, non-crystallizable ones, and that the blends of *i*PP/PE consist of semicrystalline homopolymers, to both of them one cannot apply successfully the concept of the “floating effect” for explanation of the deviations from the additivity law (Eq. (1)) with the assumption $H^s = 0$. The concept of the “diluting effect”, i.e. the domination of the plastic deformation mechanism of the solid particles, seems to be more appropriate. The reason for this is, as stated in the preceding section, the fact that the dominating (in amount) solid particles (crystalline or amorphous ones) form the matrix, in which is dispersed the minor in amount soft component and/or phase.

From the comparison of these two different (with respect of crystallinity) systems, one can conclude that for the explanation (and overcoming) the frequently observed deviations from the additivity law (Eq. (1) assuming $H^s = 0$), the crystal characteristics (crystal sizes, crystal free surface energy, etc.) are not of basic importance. What counts in this case is the mechanism of deformation of the solid particles under the indenter, i.e. if one deals *only* with their plastic deformation under the indenter (the case of “diluting effect”) or with the same mechanism, however, *paralleled* by a displacement of the solid particles in the soft matrix (the case of “floating effect”). The domination of one or the other deformation mechanism depends exclusively on the ratio solid/soft (liquid-like) components and/or phases and not by the fact if the solids particles are amorphous or crystalline.

Finally, the fact that the analytical relationship between T_g and H (Eq. (8)) helps to solve “the problem” regarding the deviations from the additivity law (Eq. (1)) means that the very basic starting assumption regarding the deformation mechanism, i.e. the “floating effect” of the solid particles in the dominating soft component and/or phase, is quite reasonable. This fact should be always taken into account when the mechanical behavior of such systems is considered.

Copolymers versus polymer blends

In the present section are analyzed various amorphous systems—homopolymers, their miscible blends, copolymers and their blends. This variety makes it

possible to follow the effect of presence or lack of chemical linkages between the constituent monomers, i.e. if one deals with a blend of two homopolymers or with a copolymer of the same monomers. Interesting conclusions in this respect can be drawn from the miscible blend PMMA/PVDF (Table 4). The results obtained 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 not only their microhardness but also their T_g values for any blend composition because these values can be evaluated by means of the Gordon and Taylor equation [38].

Particularly striking in the present results (Table 4) 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 behavior has been observed between blends of homopolymers and copolymers prepared from the same monomers [1, 50].

Important support of this conclusion can be found in the microhardness behavior of the glassy block copolymers of PS and PB with various architectures, their blends, as well as their blends with amorphous homopolymers (hPS).

As shown, Eq. (21) considers the blend of star-like and linear type block copolymers of PS and PB as comprising four components, the two types of blocks in the two different with respect of the molecular architecture block copolymers. The use of this equation presumes the knowledge of four T_g values (for each of the four blocks). Experimentally have been detected only two T_g , that of PS and that of PB [41]. For this reason, Eq. (21) was modified into Eq. (22) that accounted only for two glassy phases, PS and PB. The data obtained by means of Eq. (22) are satisfactory, particularly for the samples with dominating soft phase (PB), (Table 5).

Quite similar is the situation with the amorphous blends of hPS and star block copolymers of PS and PB (Table 6). This two-component system consists of homo PS and a block copolymer of PS and PB, however, again only two T_g have been experimentally revealed [42].

The cases described lead to the important conclusion that the microhardness of a complex multicomponent and/or multiphase system depends only on the

Table 7 Molecular weight, M_w , polydispersity, M_w/M_n , glass transition temperature, T_g , experimentally measured microhardness, H_{exp} , calculated microhardness (according to Eq. (8)), H_{cal} ,

and the difference between the calculated and the measured values, ΔH , of various types of PS

Material	M_w (kg mol ⁻¹) [51]	M_w/M_n [51]	T_g (°C) [51]	H_{exp} (MPa)[51]	H_{cal} (MPa) (acc. Eq. (8))	$\Delta H = H_{cal} - H_{exp}$ (MPa)
PS – 165	313	2.1	104	171	172	1
PS – 174	311	2.5	105	176	174	2
PS – 177	317	2.6	106	178	176	2
PS – 179	316	2.8	111	185	186	1

number of the actually observed components and/or phases (on their individual microhardness values and their respective mass fraction), regardless of whether these components and/or phases consist of homopolymer(s), their blends or parts (blocks) of copolymers. It seems that for amorphous polymer systems the microhardness depends exclusively on the chemical composition and structure of a specific monomer, but not on the type of chemical linkages (homo- or copolymers) in agreement with our former observations [1, 50].

New data on the relationship between H and T_g of amorphous polymers

Since the publication of the equation relating H and T_g of amorphous polymers in 1999 [13], new data about the microhardness values were published. This include results on PS materials with various molecular architectures (highly branched) displaying some higher T_g values as compared to the linear PS [51].

Samples of glassy PS with different amounts of long branches have been investigated (PS-165 is a linear PS, and the amount of branches for samples PS-174, PS-177, and PS-179 increases with the number code) [51]. The molecular weight, polydispersity, glass transition temperature, and microhardness data of these materials are listed in Table 7.

A fair agreement between the measured, H_{exp} , values [51] and those calculated by means of Eq. (8) ones for H_{cal} can be observed (Table 7). This fact confirms the validity of Eq. (8) for the group of amorphous polymers (characterized by dominating single, mostly C–C bonds). In addition, one can again

conclude from the results in Table 7 that the molecular architecture does not affect the validity of Eq. (8).

With regard to the future development of the present study it seems important to mention that Eq. (8) was recently modified in such a way that it accounts also for the temperature dependence of H for amorphous polymers [52]:

$$H^T = 1.97T_g - 0.6T - 395(\text{MPa}), (T_g \text{ and } T \text{ in K}) \quad (23)$$

where H^T is the microhardness value at the test temperature T .

In other words, the microhardness of the same group of amorphous polymers, covered by Eq. (8), can be calculated for any temperature T below T_g if T_g is known. The experimentally derived Eq. (23) based on results for 4 amorphous polymers, (PS, PMMA, PEN and PET) was recently verified by the reported data on the temperature dependence of H for PMMA synthesized by radiation polymerisation [53]. In Table 8 the experimentally measured H_{exp}^T values at various temperatures, (ranging between 15 and 78 °C) are compared with the calculated ones, H_{cal}^T , applying Eq. (23).

A quite good agreement between the two types of values can be found. What is striking in this case, is the observation that the difference between H_{cal}^T and H_{exp}^T tends to zero with increasing temperature of measurements, T . This could mean that T_g , being indicative for the viscosity of the amorphous material, is getting more sensitive with this respect when the test temperature T approaches the softening point, T_g .

In the same paper [53] careful measurements of H^T have been performed in the same temperature interval

Table 8 Measured microhardness values, H_{exp}^T , and the calculated ones, H_{cal}^T , according to Eq. (23), as well as the difference, $\Delta H^T = H_{cal}^T - H_{exp}^T$, for various test temperatures, T , of glassy PMMA

T (K)	288	299	312	317	324	330	335	338	340	342	344	347	350	351
H_{exp}^T (MPa)	161	141	132	127	120	117	111	109	107	105	101	97	95	91
H_{cal}^T (MPa)	132	124	117	114	110	106	103	101	100	99	98	96	95	93
ΔH (MPa)	-29	-17	-15	-13	-10	-11	-8	-8	-7	-6	-3	-1	0	2

The measured by DSC T_g value of PMMA is reported to be 354 K [54]

Table 9 Measured microhardness values, H_{exp}^T and the calculated ones, H_{cal}^T according to Eq. (23), as well as the difference $\Delta H^T = H_{\text{cal}}^T - H_{\text{exp}}^T$ for various test temperatures, T , of blend of

T (K)	288	300	312	317	324	330	335	338	340	342	345	347
H_{exp}^T (MPa)	128	121	113	110	106	103	99	98	96	95	93	92
H_{cal}^T (MPa)	115	108	101	101	100	100	92	94	92	92	91	90
ΔH (MPa)	-13	-13	-12	-9	-6	-3	-7	-4	-4	-3	-2	-2

glassy PMMA with natural rubber (up to 5 wt%). The measured by DSC T_g value of PMMA is reported to be 354 K [54]

for the blend PMMA/natural rubber (NR), the latter being in amount of up to 5 wt%. The blend films have been prepared from a common solvent [53]. In the next Table 9 are presented the data on H_{exp}^T (as reported in [53]), and the 23 H_{cal}^T values calculated by means of Equation.

Surprisingly, again a fair well agreement between H_{cal}^T and H_{exp}^T values can be seen, particularly with the progress of the test temperature (for two-thirds of a total of 12 measurements, the difference $\Delta H^T = H_{\text{cal}}^T - H_{\text{exp}}^T$ amounts to between 2 and 6 MPa), which, occasionally, correspond to the same percentage of deviations (Table 9).

Taking into account the results presented in the last two Tables 8 and 9, it sounds challenging to study to what extent Eq. (23) can be applied to complex polymer systems comprising dominating soft component and/or phase, i.e. if it would be possible to predict the overall microhardness of such systems for any temperature below T_g and/or T_m of the solid component and/or phase without experimental measurements. Such an expectation seems feasible, as long as the T_g value of the soft component and/or phase account for the changes in their viscosity according to Eq. (23), as demonstrated by the data summarized in Tables 9.

As a matter of fact, the verification of this expectation is the target of the next step of this study.

Modified additivity law for systems containing soft component and/or phase

Coming back to the main goal of the present study, the application of the additivity law (Eq. (1)) to complex polymer systems containing soft component and/or phase, we would like to suggest its modification by incorporating the relationship between H and T_g (Eq. (8)). The advantage of this modification consists in the possibility to use it for accounting for the contribution of any amorphous phase and/or component to the overall microhardness of the system, provided the T_g value of this phase and/or component is known, regardless of their value. Hence, for systems, which contain more than one crystalline and/or amorphous phases with crystalline microhardness, glass transition

temperatures and mass fractions H_{ci} , T_{gi} and ϕ_i , respectively, the additivity law can be presented in the following way:

$$H = \sum \phi_i w_{ci} H_{ci} + \sum \phi_i (1 - w_{ci}) (1.97 T_{gi} - 571) \quad (24)$$

For systems where the solid (hard) components and/or phases are not crystallizable materials, Eq. (24) can be simplified as:

$$H = \sum \phi_i (1.97 T_{gi} - 571) \quad (25)$$

In these two last forms, contrasting to the traditional one (Eq. (1)), the additivity law is applicable to multicomponent or multiphase systems comprising soft components or phases displaying a more complex deformation mechanism than the case in which all the components and/or phases have T_m and T_g above room temperature.

Conclusions

Using the reported data on the experimentally derived values of the glass transition temperature, T_g , degree of crystallinity, w_c , Vickers indentation microhardness, H , and blend compositions for homopolymers, block copolymers, blends of polyolefins, or of polycondensates, blends of miscible amorphous polymers and copolymers (some of them with rather complex molecular architecture), all of them containing a soft at room temperature component and/or phase, an attempt is undertaken to look for the reasons for the frequently reported drastic deviations of the experimentally derived H values from the calculated ones by means of the additivity law assuming that the contribution of the soft component and/or phase is negligibly small.

In contrast to this commonly used approach, it is suggested in the present study that the soft component and/or phase can dramatically change the deformation mechanism under the indenter, and thus to contributor significantly to the formation of the overall H value. It

is demonstrated that this contribution can be quantitatively accounted for via the empirically derived relationship between H and T_g . The above disclosed results allows one to derive the following conclusions:

1. The additivity law can be successfully applied also to complex polymer systems comprising soft component(s) and/or phase(s) if one accounts for their contribution to the overall microhardness of the system via their T_g and applying the linear relationship between H and T_g derived from solid amorphous polymers [13]. In this way one takes into account the fact that the deformation mechanism under the indenter is rather different compared to the systems distinguished by T_g and T_m values being above the ambient temperature.
2. This approach allows one to overcome to some extent the main disadvantage of the indentation technique for measuring H , the necessity to obtain observable, well defined indentation impressions on the sample surface.
3. The microhardness behavior of blends of completely amorphous homo- and copolymers supports our previous conclusion [1] that the contribution of a component and/or phase to the overall microhardness depends mostly on the chemical nature of the respective monomers. Whether the monomers are chemically linked giving a homopolymer, a copolymer (even with a complex molecular architecture) or one deals with blends of them does not play any significant role.
4. In contrast to the “floating effect” concept, the application of the thermodynamic approach (accounting for the crystal sizes, crystal surface free energy, etc.) for the explanation of the deviations from the additivity law is possible only for systems comprising crystalline component and/or phase; what is more, even for the last systems, the calculation of H requires the knowledge of parameters which are not easily accessible.
5. A modified additivity law is suggested which contains a term accounting for the contribution of the soft component and/or phase to the overall microhardness via the relationship between H and T_g ; its application results in much smaller differences between the measured and calculated H values.

Acknowledgements The author would like to thank Prof. F. J. Balta Calleja from the Instituto de Estructura de la Materia, CSIC, Madrid, Spain, for his stimulating discussions on the disclosed topic, as well as Prof. D. Rueda from the same Institute for reading the manuscript and for his valuable suggestions. Thanks are also due to Mag. Chem. M. Boyanova for her

technical help during preparation of manuscript. The author acknowledges also the financial support of the Foundation for Research, Science and Technology of New Zealand, making possible his stay at the Department of Mechanical Engineering and the Centre for Advanced Composite Materials of The University of Auckland, Auckland, New Zealand, where this study was finalized. The hospitality of The University of Auckland is also acknowledged.

References

1. Balta Calleja FJ, Fakirov S (2000) Microhardness of polymers. Cambridge University Press, Cambridge
2. Jawhai T, Merino JC, Rodriguez-Cabello JC, Pastor M (1993) *Polymer* 34:1613
3. Osawa S, Porter M (1996) *ibid* 37:2095
4. Kiely JD, Hwang RQ, Houston JE (1998) *Phys Rev Lett* 81:4424
5. Lee EH, Rao GR, Mansur LK (1996) *Trends Polym Sci* 4:229
6. Briscoe BJ, Sebastian KS (1996) *Proc R Soc Lond A* 452:439
7. Eyerer P, Lang G (1972) *Kunststoffe* 62:222
8. Balta Calleja FJ (1994) *Trends Polym Sci* 2:419
9. Balta Calleja FJ (1985) *Adv Polym Sci* 66:117
10. Balta Calleja FJ, Santa Cruz C, Bayer RK, Kilian HG (1990) *Colloid Polym Sci* 268:1
11. Apostolov AA, Boneva D, Balta Calleja FJ, Krumova M, Fakirov S (1998) *J Macromol Sci Phys* B37:543
12. Balta Calleja FJ, Fakirov S, Roslaniec Z, Krumova M, Ezquerria TA, Rueda DR (1998) *J Macromol Sci Phys* B37:219
13. Fakirov S, Balta Calleja FJ, Krumova M (1999) *J Polym Sci Polym Phys Ed* 37:1413
14. Brandrup J, Immergut EH (1989) *Polymer Handbook*. John Wiley and Sons, New York
15. Geil PH (1987) In: Keinath SK, Miller RL, Rieke JK (eds) *Ultraquenching, double T_g , order, and motion in amorphous polymers, in Order in the Amorphous “State” of Polymers*, Plenum, p 83
16. Breedon Jones J, Barenberg S, Geil PH (1979) *Polymer* 20:903
17. Lam R, Geil PH (1978) *Polym Bull* 1:127
18. Lam R, Geil PH (1981) *J Macromol Sci Phys* B20:37
19. Miyaji H, Geil PH (1981) *Polymer* 22:701
20. Perena JM, Martin B, Pastor M (1989) *J Mater Sci Lett* 8:349
21. Popli R, Glotin M, Mandelkern L, Benson RS (1984) *J Polym Sci Polym Phys Ed* 22:406
22. Gonzales CC, Perena JM, Bello A, Martin B, Merino JC, Pastor JM (1989) *J Mater Sci Lett* 8:1418
23. Lorenzo V, Benavente R, Perez E, Bello A, Perena JM (1993) *J Appl Polym Sci* 48:1177
24. Fakirov S, Krasteva B (2000) *J Macromol Sci Phys* B39:297
25. Boyanova M, Fakirov S (2004) *Polymer* 45:2093
26. Sperling LH (1986) *Introduction to Physical Polymer Science*. Wiley-Science, New York
27. Legge NR, Holden G, Schroeder HE (eds) (1987) *Thermoplastic elastomers. A Comprehensive Review*. Hanser, Munich
28. Roslaniec Z, Ezquerria TA, Balta Calleja FJ (1995) *Colloid Polym Sci* 273:58
29. Giri L, Roslaniec Z, Ezquerria TA, Balta Calleja FJ (1997) *J Macromol Sci Phys* B36:335
30. Ania F, Martinez-Salazar J, Balta Calleja FJ (1989) *J Mater Sci* 24:2934

31. Pietkiewicz D, Roslaniec Z (1999) *Polimery* 44:115
32. Flores A, Pietkiewicz D, Stribeck N, Roslaniec Z, Balta Calleja FJ (2001) *Macromolecules* 34:8094
33. Fakirov S, Boneva D, Balta Calleja FJ, Krumova M, Apostolov AA (1998) *J Mater Sci Lett* 17:453
34. Martinez-Salazar J, Canalda Camara JC, Balta Calleja FJ (1991) *J Mater Sci Lett* 26:2579
35. Noland JS, Hsu NNC, Saxon R, Schmitt JM (1971) *Adv Chem Ser* 99:15
36. Jungnickel BJ (1996) In: Salamone JC (ed) *Polymeric materials encyclopedia*, vol 9. CRC Press, Boca Raton, p 7115
37. Fakirov S, Balta Calleja FJ, Boyanova M (2003) *J Mater Sci Lett* 22:1011
38. Gordon M, Taylor JS (1952) *J Appl Chem* 2:493
39. Plazek DJ, Hgai KL (1996) In: Mark JE (ed) *Physical properties of polymers handbook*. American Institute of Physics, Woodbury New York, p 139
40. Simov D, Fakirov S, Mikhailov M, *Kolloid Z* (1970) *Z Polym* 238:521
41. Adhikari R, Michler GH, Cagiao ME, Balta Calleja FJ (2003) *J Polym Eng* 23:177
42. Michler GH, Balta Calleja FJ, Puente I, Cagiao ME, Knoll K, Henning S, Adhikari R (2003) *J Appl Polym Sci* 90:1670
43. Balta Calleja FJ, Cagiao ME, Adhikari R, Michler GH (2004) *Polymer* 45:247
44. Wunderlich B (1990) *Thermal analysis*. Academic, Boston
45. Lide DR (1994). *CRC handbook of chemistry and physics*. CRC Press, Boca Raton FL
46. Rueda DR, Balta Calleja FJ, Hidalgo A (1974) *Spectrochim Acta* 30a:1545
47. Martinez-Salazar J, Balta Calleja FJ (1980) *J Cryst Growth* 48:283
48. Gonzales Ortega JC, Balta Calleja FJ (1974) *An Fiz* 70:92
49. Martinez-Salazar J (1979) PhD Thesis, Universidad Autonoma de Madrid, Madrid Spain
50. Fakirov S, Krumova M, Rueda DR (2000) *Polymer* 42:3047
51. Balta Calleja FJ, Giri L, Esquerra TA, Fakirov S, Roslaniec Z (1997) *J Macromol Sci Phys* B36:655
52. Garcia Gutierrez MC, Michler GH, Henning S, Schade C (2001) *J Macromol Sci-Phys* B40:795
53. Fakirov S, Krumova M, Krasteva B (2000) *J Mater Sci Lett* 19:2123
54. Mina MF, Ania F, Balta Calleja FJ, Asano T (2004) *J Appl Polym Sci* 91:205