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The asymmetrical orientational behavior of compatible blends of PMMA and PVC*)

M. Grell[1]) and J. H. Wendorff[2])

[1]) Deutsches Kunststoff-Institut, Darmstadt, FRG
[2]) Fachbereich Physikalische Chemie und Wissenschaftliches Zentrum für Materialwissenschaften, Philipps-Universität Marburg, FRG

*) *Dedicated to Prof. E.W. Fischer on the occasion of his 65th birthday*

Abstract: The orientation and relaxation behavior of compatible blends of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC) was investigated. The deformation was performed at 9 K above the glass transition temperature. Based on birefringence and IR-dichroic measurements, it was found that the orientation of PMMA is strongly increased in the blends as compared to pure PMMA at identical draw ratios.

The orientation of PVC, on the other hand, is not changed by blending. The results are discussed in terms of friction coefficients and their enhancement by molecular interactions.

Key words: Orientation – relaxation – PMMA – PVC – glass transition

I. Introduction

The deformation of polymer melts gives rise to an elongation of the coiled molecules which in turn leads to an orientation of their segments. Optical birefringence measurements, dichroic studies or x-ray investigations can be used among other methods in order to characterize the induced orientational order. The chain deformation, on the other hand, gives rise to a restoring force which is predominantly of entropic nature: the deformation tends to relax as the force is removed.

An interesting problem both with respect to fundamental and applied science is the deformation and relaxation behavior of compatible blends of chain molecules. This paper is concerned with a binary blend of chemically different polymers, namely, PMMA and PVC.

Several papers have addressed the deformational behavior of homogenous blends [3–5, 7]. The results were that distinctly different types of orientational behavior may occur for the pure blend components as compared to the ones of the same polymer blended with different partners. The orientational behavior of blends ranges from an extremely asymmetrical case – as in PVME/PS [3] where PVME is not oriented at all and where the orientation of PS is increased by blending – to an almost symmetrical case – as observed for the system (PS/PPO [4]) where PS orientation is affected by the presence of PPO almost in the same way as PPO orientation is affected by PS.

These results were discussed by the authors on the basis of the friction coefficient. The friction coefficient does not only depend on the respective polymer chains in blends, but also on the coupling to their surrounding, the strength of which is controlled by the interaction parameter. The central point in this interpretation consequently is that a negative interaction parameter gives rise to an enhanced friction coefficient as compared to the pure polymers systems. The friction coefficient, in turn, sets the time scale of the orientational relaxation process. In the case of $\chi \approx 0$, there is no effect of blending on the orientational properties [5].

For a more quantitative discussion, one has to focus on the relevant length scale in this type of experiment. The characterization of the orientation by spectroscopic methods reveals information on the segmental scale. The orientational and relaxational properties are in general very different on the entanglement network scale as compared to the segmental scale. The deformation on the entanglement scale is characterized simply by the macroscopic elongation if an oriented sample recovers its initial length on heating above T_g, no irreversible processes have occurred on the entanglement scale in this case. However, this does not necessarily mean that the orientation on the segmental scale is controlled simply by the elongation, too. The deformation behavior in this regime was termed "macroelastic", but also "microviscous" by Picot et al. [4]. Even if the segmental orientation parameter

$$\langle P_2 \rangle = 2 \int_0^{\pi/2} f(\vartheta) P_2(\cos \vartheta) \sin \vartheta d\vartheta$$

(P_2 is the second Legendre Polynom, $f(\vartheta)$ the distribution function of the segmental axis) equals zero, the polymer chain may be in a conformation far from equilibrium [8].

The segmental orientation is then supposed to be governed by microscopic parameters, in particular by the monomeric friction coefficient. This point of view is corroborated by Lefebvre et al. [10], who showed that the orientation of PPO in PPO/PS- blends is independent of the molecular weight of PPO as long as it is larger than the entanglement molecular weight. This is consistent with the assumption that the orientational properties are governed by the monomer and not the polymer friction coefficient.

This impact of the monomer friction coefficient gives rise, however, to an ambiguity in the quantitative analysis of the experimental results as far as polymer blends are concerned. The friction coefficients depend strongly on the difference between the actual temperature and the glass transition temperature; they may vary for example by about seven decades within a temperature interval of 90 K as found for PS [6]. On the entanglement scale, the mobility of the system is governed by the common T_g of the blend, but it is not a priori apparent whether the segmental reorientation processes are governed by the common or the individual glass transition temperatures.

In the compatible blends of PVME/PS [3] and PEO/PMMA [7], one can rationalize the zero segmental orientation on elongation of PVME and PEO if one takes the low T_g's of these components (PVME: $T_g = -82$ C [11]) as a basis for estimating the values of the friction coefficients. The low friction coefficients at the elongation temperature will result in a complete relaxation on the experimental time scale.

However, in the case of PS/PPO-blends the PS orientation is enhanced by blending with PPO [4] although its glass temperature is about 100 °C lower than that of PPO [11]. The friction coefficient of PS is not extraordinarily high [15] and the interactions in PS/PPO are not extraordinarily strong [16]. If one tends to keep the simple model introduced above, one has to postulate a strong influence of the localization of interactions on the friction coefficient. One has to assume for instance that the bulky PS phenyl ring with its π-electron system leads to localized interactions and thus to strong restrictions in motions.

In the investigations reported in this paper, we have tried to avoid the ambiguity in the choice of the relevant T_g as far as possible by choosing a blend system characterized by components having similar T_g's. On the other hand, we wanted to choose a system where the two components display very different monomeric friction coefficients, in order to study the role of the friction coefficients during the orientation. Finally, the choice was directed by the aim to study systems characterized by strong interactions (negative interaction parameter) and by a broad concentration range for which compatibility was realized. The last two features are, of course, implicitly connected. The system PMMA/PVC turned out to be a good choice. The difference in T_g of about 25 °C cannot mask the difference of the intrinsic friction coefficients; the PMMA friction coefficient is about five decades higher than that of PVC at 125 °C [15]. The high PMMA friction coefficient is attributed to the bulky methyl groups [15] which are strongly engaged in specific interactions with PVC. Due to the strong interactions one expects an influence of blending on the orientational behavior of PMMA.

The orientational behavior of PVC on the other hand is expected to show some unusual features in the blends. The reason is that the segmental orientation of PVC can become as high as in liquid crystalline substances ($\langle P_2 \rangle \approx 0.5$ [17]). This may be regarded as some evidence for a "quasi-nematic" structure of PVC which has been postulated by some authors [19, 20]. It is not a priori known whether PVC blended with PMMA will orient poorly due to its low intrinsic friction coefficient or whether the strong interactions with PMMA will give rise to a strongly enhanced friction coefficient in blends resulting in a nonvanishing PVC orientation.

II. Methods of analysis

Uniaxial stretching of a polymer in the viscoelastic state above T_g results in a preferred orientation of the chain segments along the stretching direction. This orientation can be transferred into the glassy state and thereby stabilized by rapidly cooling the sample below its T_g while keeping its ends fixed to prevent relaxation. Uniaxial deformation causes an orientation displaying an azimuthal and inversion symmetry which may therefore be characterized by the orientation parameter $\langle P_2 \rangle$. This also is the easiest one to be determined experimentally. We have studied this quantity using IR-spectroscopy and birefringence measurements.

Birefringence

Birefringence couples to $\langle P_2 \rangle$ according to: [12]

$$\Delta n_{\mathrm{or}} = \langle P_2 \rangle \Delta n_{\mathrm{intrinsic}} \tag{1}$$

where $\Delta n_{\mathrm{intrinsic}}$ is the (hypothetical) birefringence of the perfectly aligned state.

However, in the particular case of oriented polymers in the glassy state, there are some cautionary remarks to be made about the use of birefringence measurements to evaluate $\langle P_2 \rangle$.

Orientational birefringence is not the only contribution to the total birefringence. Frozen-in shear stresses exist for quenched samples resulting from an inhomogenous cooling across the glass transition range for surface- and bulk volume elements. In addition, one has to take into account that the frozen-in orientation gives rise to entropic stresses within the material. Both stresses cause birefringence, the entropic contribution varying linearly with the absolute temperature as reviewed by Struik [1].

Another difficulty lies within the intrinsic birefringence $\Delta n_{\mathrm{intrinsic}}$. $\Delta n_{\mathrm{intrinsic}}$ is not a priori known and may vary with temperature as pointed out by Wimberger-Friedel [2] for the case of PMMA above T_g.

In blends, the resulting orientation birefringence is given by a weighted average over the constituents: [12]

$$\Delta n_{\mathrm{or}} = \Phi(1)\langle P_2^{(1)} \rangle \Delta n^{(1)}_{\mathrm{intrinsic}} + \Phi(2)\langle P_2^{(2)} \rangle \Delta n^{(2)}_{\mathrm{intrinsic}} \tag{2}$$

$\Phi(\mathrm{i})$ is the volume fraction.

In the context of this paper it will become apparent that the $\langle P_2{}^{(1,2)} \rangle$ may depend on Φ. The respective values at the same elongation for the pure polymers thus cannot be used for the blends. Even if the non-orientational birefringence contributions are correctly taken into account, the evaluation of the orientation of one of the constituents in a homogenous blend is possible only if both $\Delta n_{\mathrm{intrinsic}}$ and the orientation of the other constituent are known.

In many previous studies on birefringence and orientation, the temperature dependence of the birefringence was ignored [3–7, 17]. Nevertheless, the results remain useful if the orientational entropy varies linearly with $\langle P_2 \rangle$ since the apparent intrinsic birefringence is altered linearly by temperature, too, exactly compensating the error made by ignoring thermal effects on birefringence. However, if other thermal effects (like a temperature-dependent intrinsic birefringence) have to be taken into account the compensation fails.

IR Spectroscopy

Using vibrational (IR-) spectroscopy the value of $\langle P_2 \rangle$ is obtained directly with no a priori unknown contributions entering the analysis.

For any absorption band, the dicroic ratio $D = E_p/E_0$ ($E_{p/0}$: Extinction parallel/orthogonal to stretching axis) is related to $\langle P_2 \rangle$ by [12]:

$$\langle P_2 \rangle = \frac{D-1}{D+2}\,\frac{D_0+2}{D_0-1}\,, \tag{3}$$

where $D_0 = 2 \cot^2\beta$, and where β is the angle between the dipole moment vector of the vibration and the segmental axis.

In polymer blends, one can determine the orientation of any of the constituents separately if one finds a dicroic absorption band. In the case of PMMA, it is known from the literature [7] that the 749 cm^{-1} absorption band is well suited for dicroism measurements, its transition moment making an angle of 17° with the segmental axis. Since there is no PVC band overlapping, this band was used to characterize the orientation of PMMA in this investigation.

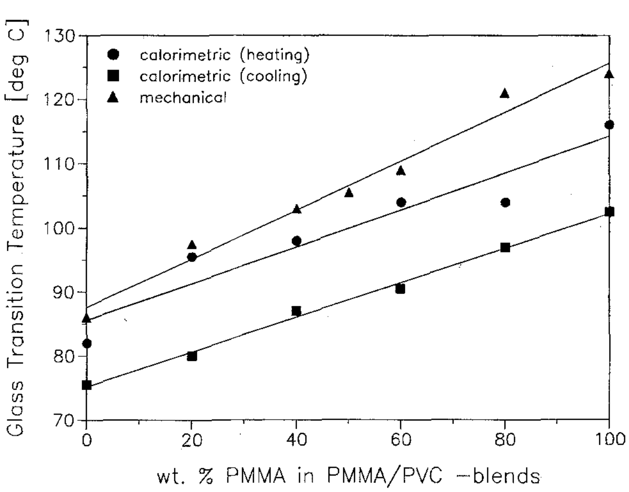


Fig. 1. Glass transition temperatures vs blend composition due to different methods

III. Experimental

Samples

The polymers used were commercial products as supplied by Röhm AG (PMMA) and Hüls (PVC). The PVC was slightly modified by a thermal stabilizer and processing agents. Data are given by Table 1.

The blends were mixed in a Brabender plasticizer at 170 °C and re-granulated by a mill. To obtain samples suitable for uniaxial stretching, we used a metal stencil to mould the granulate at about 170 °C into a bar-like shape. The samples were subsequently annealed for 1 day at 130 °C in order to relax residual stresses and orientations resulting from the thermochemical history of the samples. The samples were found to be almost free of residual birefringence ($\Delta n < 5*10^{-5}$) after the annealing procedure.

Determination of the glass transition of the blends

In order to select appropriate deformation temperatures we determined the glass transition temperatures of the pure components and the blends. We used a Perkin-Elmer DSC 4 for calorimetry and a Myrenne torsion pendulum for shear modulus measurements.

Heating and cooling rates for calorimetry were 20 K/min, the frequency of mechanical testing was 1 Hz. The values of T_g were taken to be either the midpoints of the steps in heat capacity as evaluated by the Perkin-Elmer thermal analysis software or the damping maxima in the mechanical experiments, respectively. The results are shown in Fig. 1.

By finding just one T_g for any composition, we confirmed the homogenity of our blends. As a basis for our elongation program we chose the glass transition temperatures as determined by the torsion pendulum method.

Orientation procedure

For orienting polymers effectively, we selected a temperature high enough above T_g in order to be

Table 1. Materials used for this investigation. M_w was measured with PS calibration. All additives were supplied by Ciba-Geigy.

Polymer	Producer	Type	Additives	M_w	Polydispersity
PMMA	Röhm	Plexiglas 8N	None	119000	1.97
PVC	Hüls	Vestolit S 7054	Irgastab 17M 2 wt.% Irgawax 360 1 wt.% Irgawax 361 1 wt.%	165000	2.17

able to elongate them without destruction to a reasonable drawing ratio (about 3–5) but on the other hand low enough to prevent stress relaxation on the time scale of the drawing procedure. A reasonable choice of drawing parameters turned out to be a choice of a temperature $T_{\text{draw}} = T_g$ (Pendulum) + 9 K and of a constant drawing speed of 50 mm/min, for an initial free length of the bars of 5 cm resulting in a nominal drawing rate of 0.017 s^{-1}. The samples were drawn by a Zwick mechanical testing apparatus equipped with a hot-air heat chamber. Before drawing, a scale was painted on the samples to characterize draw ratios afterwards.

After finishing the drawing process the heat chamber was instantaneously flooded with air at room temperature, thus cooling the samples quickly well below their glass transitions. Several bars of every composition were drawn to different ratios up to the breaking limit.

To avoid drawing ratio gradients in the samples we cut out the middle part of the resulting bars where the drawing ratio was approximately homogenous. When re-heating such samples to about 50 K above the glass transition all of them recovered their initial length within the experimental errors. From this observation, we concluded that no relaxation processes on the scale of the entanglement network have occurred during the drawing procedure.

Birefringence measurements

We used a Leitz polarizing microscope equipped with a tilt compensator and a hot stage to determine the drawing ratio and temperature dependent birefringence. The temperature at which the measurements were performed was kept well below T_g to prevent a thermally induced relaxation creep. It was carefully checked that all results could be reproduced for several heating and cooling cycles.

IR-dichroic measurements

For IR-dichroism experiments, we used thin (10–50 μm) samples. These samples were cut from our bars by a microtome with a glass knife. We selected samples having an area of about (5 × 1) mm^2 from the central part of the bars to examine the bulk orientation properties and to avoid possible inhomogenities at the bar's edges.

We used a Nicolet 60 SX FTIR spectrometer equipped with a wire grid polarizer and a simple slit- device to adapt the samples to gain dicroic spectra from the 749 cm^{-1} band of PMMA. For a good signal-to-noise ratio, 500 spectrometer scans were oversampled.

IV. Results

Birefringence

Figure 2 shows the dependence of the birefringence on the elongation $\lambda = l/l_0$ and the temperature below the glass transition temperature for the pure components and for different compositions in a three-dimensional representation. Note the negative sign of Δn for 100% PMMA.

The results for pure PVC are the easiest to understand; we observe a birefringence which increases for increasing elongation as expected for an orientation increasing with elongation. For a given elongation, the birefringence varies linearly with temperature due to frozen-in entropic stresses as reviewed by Struik [1]. An extrapolation of these straight lines to $T = 0$ K for $\lambda \approx 3$ shows that about 50% of the birefringence at room temperature originates from entropic stresses; only the remaining 50% are to be ascribed to orientation birefringence.

In pure PMMA, for a fixed temperature the absolute value of birefringence rises with elongation, too; the sign is negative due to a negative segmental anisotropy. The temperature dependence of birefringence is, however, more complex. This may be understood by assuming a temperature-dependent intrinsic birefringence of PMMA (see discussion).

The birefringence results are even more complex in blends. The most striking example is the 80% PMMA/20% PVC blend, where for higher elongations the birefringence shows a local minimum at about 60 °C.

IR Dichroism

The results of IR-dichroic measurements are presented in Fig. 3.

Figure 3 shows the dependence of $\langle P_2 \rangle$ on elongation for pure PMMA and for PMMA

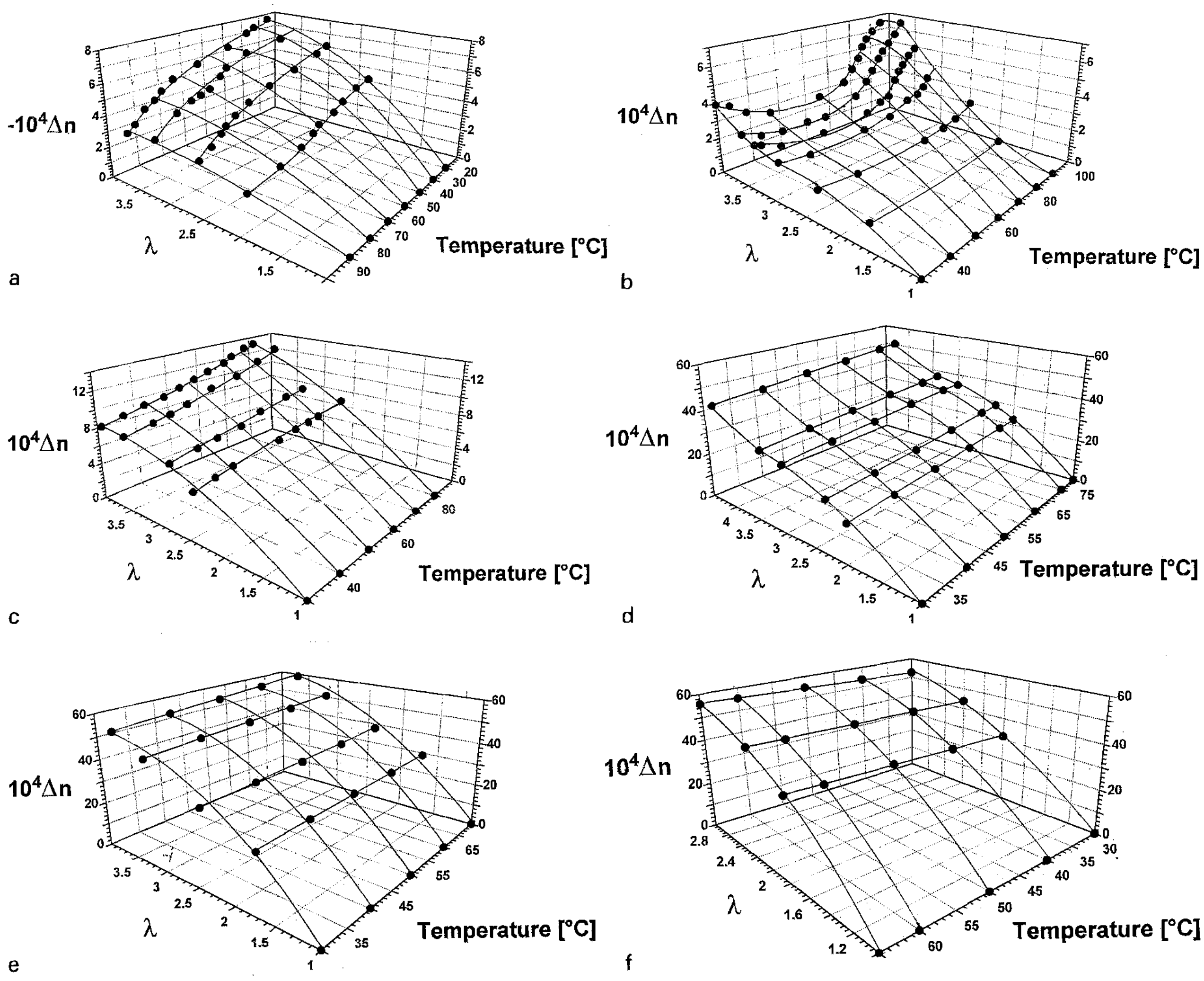


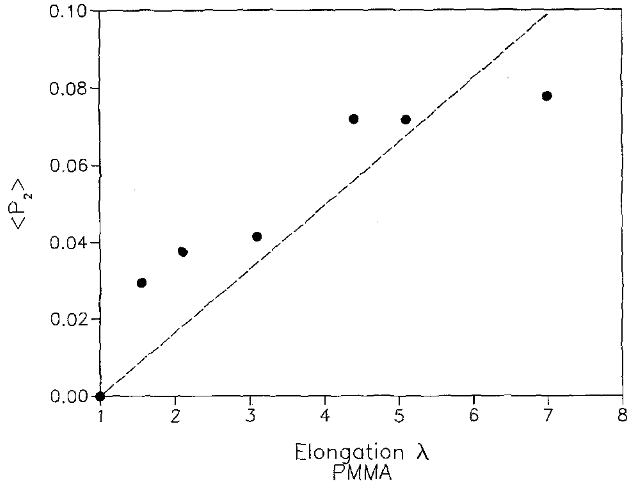
Fig. 2. Birefringence vs T and λ for different blend compositions; 2a 100% PMMA; 2b 80% PMMA/20% PVC; 2c 60% PMMA/40% PVC; 2d 40% PMMA/60% PVC; 2e 20% PMMA/80% PVC; 2f 100% PVC

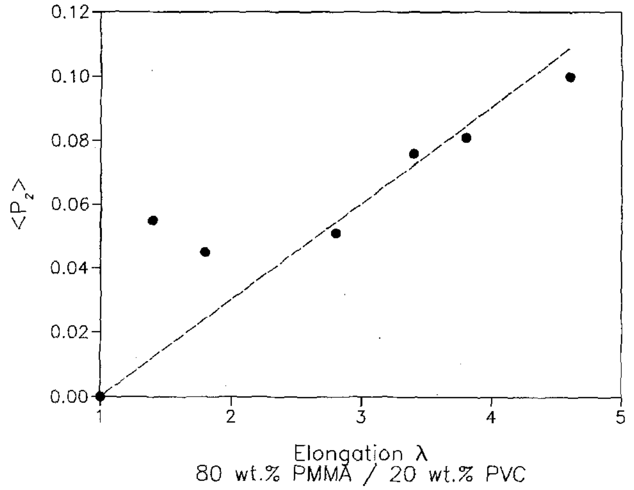
blended with different amounts of PVC. The values for the pure PMMA lie within the same order of magnitude as those reported in [18] for similar investigations. We have fitted straight lines to the data according to

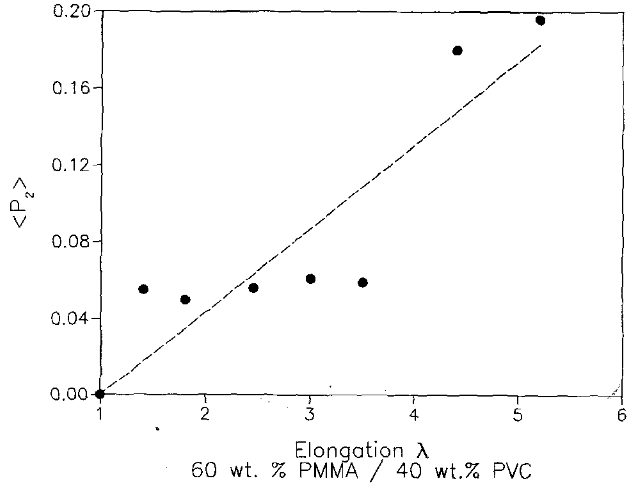
$$\langle P_2 \rangle = C*(\lambda - 1) \qquad (4)$$

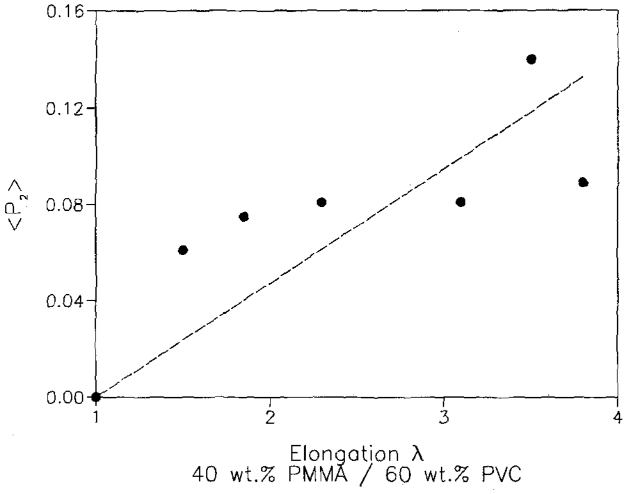
We have termed the slope C of these lines as "orientation coefficient". The deviation of single points from the fits is a consequence of (3) boosting experimental and data sampling (baseline fitting!) errors.

By averaging the data by fitting straight lines and plotting their slopes (orientation coefficients) as a function of the composition of the blend, one obtains the results presented in Fig. 4. The orientation coefficient of PMMA increases linearly with increasing content of PVC in the blends; it approaches a value which is about three times as large as in pure PMMA in the limit of a PVC-concentration → 100%.









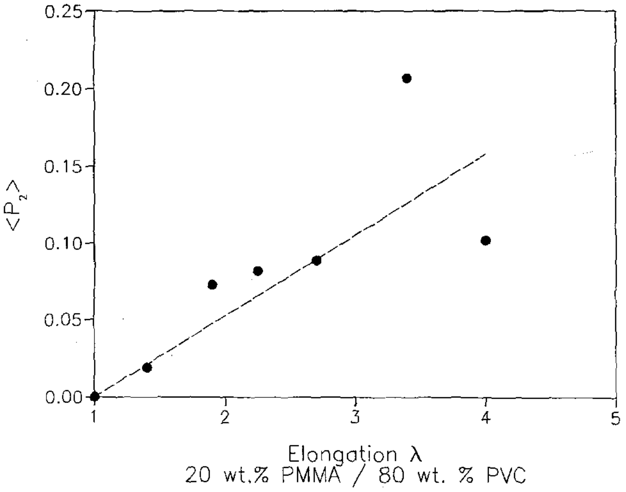


Fig. 3. PMMA Orientation parameter $\langle P_2 \rangle$ vs elongation for different blend compositions; 3a 100% PMMA; 3b 80% PMMA/20% PVC; 3c 60% PMMA/40% PVC; 3d 40% PMMA/60% PVC; 3e 20% PMMA/80% PVC

V. Discussion and conclusions

Birefringence

Pure Polymers

PVC

As pointed out in the section on results, the elongation- and temperature dependence of the birefringence of PVC samples can be understood quite easily. The values of Δn agree well with those of Hibi et al. [17] which were reported for slightly different drawing conditions. Using the intrinsic

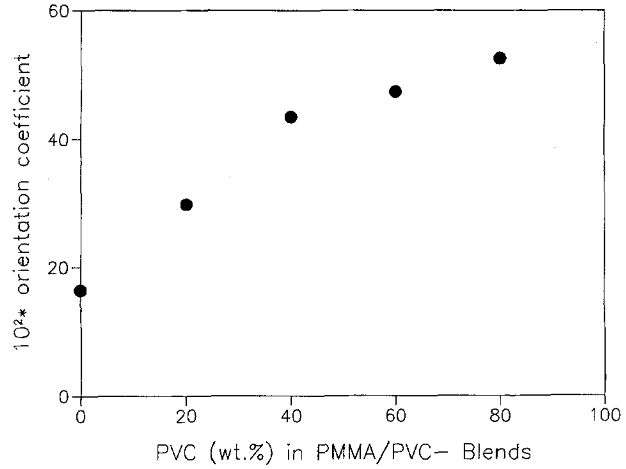


Fig. 4. PMMA orientation coefficients vs PVC content in blends

birefringence $\Delta n_0 = 104*10^{-4}$ given in [17], the maximum $\langle P_2 \rangle$ shortly before reaching the breaking limit is about 0.5. As far as we know, this is a value which is much higher than obtainable for any amorphous polymer by simple elongation. (The authors did not take into account the entropic stress birefringence, but the result $\langle P_2 \rangle$ (max) ≈ 0.5 seems to be reasonable as pointed out in the section on methods.) This can be considered as a support for the thesis that PVC shows ordering phenomena similar to those in semicrystalline or liquid crystalline polymers as discussed in [21].

PMMA

For an interpretation of the PMMA birefringence results, we have to focus on the concept of a temperature-dependent intrinsic birefringence of PMMA.

Wimberger-Friedel [2] has observed an analogous temperature dependence of the "stress optical coefficient" (SOC) for PMMA- melts, the SOC even changing sign at 144 °C. Wimberger-Friedel interpreted his result in terms of rotations of the ester groups in PMMA around the chain backbone. Since these rotations are related to the β-relaxation, which is not suppressed by the glass transition, it is reasonable to assume a temperature dependence of the intrinsic birefringence (which is the analogon of the SOC) which does not vanish below T_g.

Based on this assumption, combined with the inevitable entropic stress birefringence, one can explain the observed temperature dependence of birefringence in oriented PMMA. It should be kept in mind that even for pure PMMA it is quite difficult to extract information on $\langle P_2 \rangle$ (which below T_g does not vary with temperature) from birefringence results because of the variety of quantitatively unknown contributions to Δn.

Blends

As pointed out in the method section, the total orientational birefringence of an amorphous blend is the weighted average of the contributions of the constituents. Since the intrinsic birefringences of PMMA and PVC have different signs and since the birefringence of PMMA shows a nontrivial temperature dependence, one expects a quite complex behavior of the birefringence of the blend. It is obvious that one cannot simply add the weighted results for the pure components to obtain the corresponding blend value. For example, this procedure fails to reproduce the minimum in the 80% PMMA/20% PVC blend.

It is known from previous investigations that the orientational properties of a polymer can be affected by blending it with a compatible partner. [3, 4, 7] This implies that one has to multiply the weighted single component contributions by a factor α describing the influence of blending on the orientational properties; $\alpha = 1$ is equivalent to no effect of blending on orientational properties.

A basic problem is that one cannot extract the values of α (which, in general, will vary with blend composition) for both constituents from birefringence results alone. For this reason, we will first consider the IR-results on the orientation of PMMA which will give the quantity $\alpha_{PMMA}(\Phi)$. We will use this information to estimate the $\alpha_{PVC}(\Phi)$ by revisiting the birefringence results.

IR dicroism

In the section on results, we have presented IR-dichroic investigations on the orientational properties of pure PMMA and of PMMA blended with different amounts of PVC. Using these results, we calculated in the first step of analysis the orientation of the PMMA in the blends. The results are summarized in Fig. 4; we used them in

Table 2. Orientation of PVC in PMMA/PVC blends as obtained by combining IR and birefringence results. α were evaluated at $\lambda = 1.5, 2, 2.5, 3$; birefringence results were partly interpolated to the appropriate λ. T = 30 °C. Note that the assumption of linear variation of entropic stresses with $\langle P_2 \rangle$ is implied in this calculation.

Blend composition (wt. %)	$\langle\alpha\rangle$PVC
80% PVC/20%PMMA	1.15 ± 0.12
60% PVC/40% PMMA	1.06 ± 0.07
40% PVC/60% PMMA	0.67 ± 0.03
20% PVC/80% PMMA	1.05 ± 0.04

a second step to estimate the orientation of the PVC in the blends from the birefringence results. In the analysis, we assumed the entropic stresses to scale with the same factor α, claiming a linear relation between entropic stress and $\langle P_2 \rangle$ which seems to be reasonable to a first approximation because the entropic stresses have their origin in the anisotropic orientational distribution function $f(\vartheta)$, too.

We have found α not to depend systematically on λ, therefore the error in α was taken to be the standard deviation of the calculated α for different elongations. The results are given in table 2.

It is obvious from Table 2 that there is almost no influence of blending on the orientation of PVC. Summarizing the evidence of birefringence and IR data, we find that the orientation coefficient of PMMA is strongly enhanced in blends with PVC and that, on the other hand, the PVC orientation coefficient is almost independent of the presence of PMMA.

Conclusions

As pointed out in the introduction, the blend system PMMA/PVC was chosen for testing the theoretical concept on the segmental orientational process in polymer blends. One reason for this choice of the components was that the small difference in the glass transition temperatures makes the ambiguity between the individual T_g's and the T_g of the blend relatively unimportant for it cannot mask the large difference in the blend component's friction coefficients.

The results obtained for the orientation of the PMMA in the blend are consistent with the concept of an enhanced friction coefficient caused by a negative interaction parameter and thus by a stronger coupling to the surrounding.

The fact that pure PVC segmental orientation is different from zero despite its low friction coefficient can be accounted for by the existence of ordered structures which prevent segmental relaxation during the elongation procedure. However, in compatible blends the formation of these structures is supposed to be suppressed, nevertheless the experimental finding is that the PVC orientational parameter in blends with PMMA is about as high as for pure PVC. Therefore, one has to postulate a very strong enhancement of the friction coefficient by blending to prevent orientational relaxation during the elongation procedure.

The question is whether this is a general result. If one takes the individual glass temperatures as the basis for calculation of the friction coefficient, one has to postulate a similarly strong effect for PS in PPO/PS- blends although the interactions are not very strong in that blend [16]. One possibility might be – when insisting on the concept – that one has to accept that even the locations of specific interactions may play a crucial role in the orientational and relaxational behavior. Specific interactions giving rise to compatibility are frequently localized and direction specific.

We come to the conclusion that we are currently not able to provide a simple general rule on how to predict the orientational behavior of compatible blends based solely on the magnitude of the interaction parameter, the glass transition temperature of the blend and the properties of its components. The choice of the blend system PMMA/PVC bypasses the T_g-ambiguity, therefore it cannot resolve it.

As a concluding remark, we want to point out that more careful investigations of thermally induced relaxation creep showed [9] that the network relaxation process is governed by just one (the blend) glass temperature, the network relaxation being a more global phenomenon than the segmental relaxation. Thus the deformation of the entanglement network is reversible and completely characterized by the geometric quantity drawing ratio. The processes on the network scale are quite independent from the microscopic friction coefficient.

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Authors' address:

Dr. M. Grell
Deutsches Kunststoff-Institut
Schlossgartenstraße 6
64289 Darmstadt, FRG