# Compensation method for zero birefringence in oriented polymers

## Bernd R. Hahn* and Joachim H. Wendorff

*Deutsches Kunststoff-Institut, Schlossgartenstrasse 6R, 3-6100 Darmstadt, West Germany*
*(Received 13 December 1984)*

Optical birefringence is usually linked to molecular orientation in polymers. Birefringence in materials used for optical applications represents non-isotropic optical properties, and is therefore undesired, but cannot always be avoided. Molecular orientation was found to be possible without necessarily resulting in birefringence. This effect is achieved by combining suitable amounts of PMMA and poly(vinylidene fluoride) PVDF in the form of a compatible, amorphous blend. The observed drastic reduction in birefringence is the result of the compensation of positive and negative contributions to the overall birefringence.

## INTRODUCTION

When an isotropic polymer is oriented by drawing, the refractive index $n$ parallel to the direction of draw is no longer equal to the refractive index $n$ perpendicular to this direction and the polymer displays birefringence $\Delta n = n_{\parallel} - n_{\perp}$. The extent of birefringence depends upon the perfection of the molecular orientation and the optical anisotropy of the molecular units making up the polymer. The observation of birefringence is therefore a common experimental tool for the investigation of orientation effects in polymers[1].

Birefringence is frequently an undesired effect, if high optical quality is required (e.g. aircraft windows, optical discs, and lenses).[2] However, the requirements for good mechanical properties often lead to the need for some sort of molecular orientation, causing optical birefringence. Also, in circumstances where molecular orientation is not required *per se*, it often cannot be avoided during processing of the polymer. Processes which are designed to reduce birefringence are typically slow and more expensive.

In this paper we describe how commercially available polymers can be modified to reduce or eliminate optical birefringence. Our investigations were concerned with atactic poly(methyl methacrylate) (PMMA), because PMMA is known to possess excellent optical properties. By blending PMMA with suitable amounts of PVDF, an amorphous blend is obtainable, which remains virtually free of birefringence even after large uniaxial deformation. Our explanation of this effect agrees essentially with the one made by Prest in that PPO and PS can be blended to a birefringence-free compound[3].

## EXPERIMENTAL

PVDF resin was obtained from Solvay Company and its average molecular weights $\bar{M}_n$ and $\bar{M}_w$ are known to be 38 000 g mol$^{-1}$ and 100 000 g mol$^{-1}$ respectively (Solef X8N). The PMMA samples were obtained from Röhm

GmbH, and the values for $\bar{M}_n$ and $\bar{M}_w$ are 60 000 and 120 000 g mol$^{-1}$ respectively (PMMA 8N). Polymer mixtures were melt-blended in an extruder at 220°C three times to ensure homogeneous mixing. The resins were dried in a heat chamber before processing. Thin films of 40 to 60 $\mu$m in thickness were extruded from the blends. Also sheets of 2 mm in thickness were prepared in a hot press[4]. All the samples were found to exhibit excellent optical clarity. Samples having different blend compositions were uniaxially stretched up to different draw ratios at elevated temperatures in a Zwick-tensile machine equipped with a Brabender environmental chamber. The samples were removed and some of the samples were annealed after that. Finally the optical birefringence resulting from the stretching at different temperatures and blend compositions was determined with a Leitz polarizing microscope at 25°C[4].

## RESULTS ON OPTICAL PROPERTIES

### Refractive index

One major reason that PVDF/PMMA blends have attracted so much interest in the past is that an amorphous polymer (PMMA) and a partially crystalline polymer (PVDF) can be combined in a compatible, homogeneous blend[5-8], the properties of which depend on the composition. There have been only a few papers[9] up to now which give information on the optical properties of PVDF/PMMA blends, and the relationship between deformation and birefringence has not been published, to our knowledge.

We will consider only amorphous blends in the following, i.e. samples which have not been annealed at higher temperature and which contain a maximum weight percentage of 60% PVDF.

Firstly, we will be concerned with the refractive index. The refractive index of these PVDF/PMMA blends in dependence of the composition is shown in *Figure 1* and can be described approximately by a linear relationship. This linear relationship is not surprising, since it simply reflects the fact, that the refractive index of a polymer system can roughly be estimated by an incremental
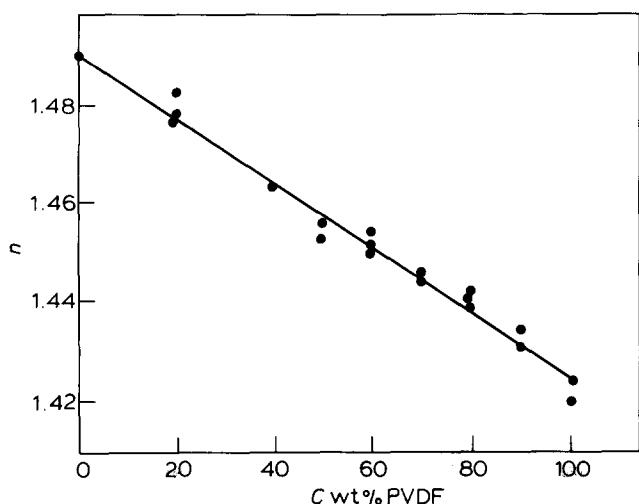
---

**Figure 1** Refractive index of PVDF/PMMA blends in dependence of their composition

method, using atomic or bond refractivities[10]. The Lorenz–Lorenz equation relates the electronic polarizability of a material to its refractive index:

$$(n^2 - 1)/(n^2 + 2) = 4\pi\rho N\alpha/3M$$

Here $\rho$ is the density, $N$ the Avogadro number and $M$ the molecular weight of the monomer unit. This equation can be applied to multiphase systems also, provided that the phase dimensions are well below the wavelength of light. This is the case for the samples studied here[11]. The refractive indices of the crystalline phase $n_c$ (averaged over all crystal orientations) and of the amorphous phase $n_a$ can be determined for pure PVDF from the densities of both phase components ($\rho_c = 2.0$ g cm$^{-3}$, $\rho_a = 1.6$ g cm$^{-3}$). One obtains $n_c = 1.48$ for the crystalline regions and $n_a = 1.37$ for the amorphous regions. The PVDF crystals thus have almost the same refractive index as amorphous PMMA ($n_{PMMA} = 1.49$). This leads to a reduction of light scattering in partially crystalline PVDF/PMMA blends, improving their transparency significantly over pure PVDF.

### Deformation-induced birefringence

The focus of this paper is strain-induced birefringence in PMMA and PVDF/PMMA blends, and how the value of birefringence depends upon the blend composition. Samples of PVDF/PMMA blends having different compositions have been stretched at different temperatures up to different draw ratios using various draw speeds of 3 cm min$^{-1}$ and 30 cm min$^{-1}$ (sample length: 7 cm). The results are shown in *Figure 2*. A nearly linear relationship between the draw ratio and the resulting birefringence after stretching is obtained for PVDF/PMMA blends having PVDF fractions between 20 and 60%. The birefringence induced depends only upon the deformation for a given composition. It does not depend upon the temperature or upon the drawing rate in the parameter range considered here. This observation indicates that PVDF/PMMA blends behave like a molecular network under those conditions, and that plastic flow does not occur during deformation to a significant extent. The maximum draw ratio, plotted in *Figure 2* for each combination of draw parameters, represents the largest deformation which could be obtained for PVDF/PMMA blends without sample failure.

The most interesting feature shown in *Figure 2* is the fact, that the slope of the dependence birefringence vs.

draw ratio becomes increasingly smaller with increasing PMMA-fraction. Obviously, only a very small birefringence is induced, even for the largest deformation possible, in a PVDF/PMMA blend having the composition 20/80. One possible interpretation for this is that no significant molecular orientation has been induced in such a blend composition. But this possibility was ruled out, after thermally induced shrinkage experiments and some qualitative dichroic i.r. absorption experiments had been done. Both experiments indicated significant molecular orientation, without birefringence.

### Compensation of birefringence

The observation of molecular orientation without birefringence, seems to be somewhat puzzling at the beginning. But a simple fact regarding birefringence has to be taken into account: birefringence can be positive as well as negative, depending upon the optical anisotropy of the segments of the polymer chain. For instance, if pure PVDF is stretched, it shows positive birefringence (i.e. $n_\parallel > n_\perp$)[7], if PMMA is stretched, it shows negative birefringence (i.e. $n_\parallel < n_\perp$[11]). In a compatible, amorphous PVDF/PMMA blend the optical properties vary continuously with blend composition. Therefore, a blend composition should exist, where positive and negative contributions to birefringence cancel each other completely, giving zero birefringence, even if high molecular orientation exists. *Figure 3* shows how to determine this composition, and compares the magnitude of birefringence for different PVDF/PMMA blend compositions for the same deformation. This should correspond to about the same molecular orientation in those different blends, assuming a network behaviour.

Most significant in *Figure 3* is the fact that a zero-crossing occurs at a blend composition of about 17/83. This means, that a PVDF/PMMA blend, having the composition 17 wt% PVDF and 83 wt% PMMA will be completely free of birefringence. A further observation is that the optical clarity of those blends is as good as that of PMMA.

### Birefringence free PVDF/PMMA blends

Assuming a homogeneous deformation and a deformation mechanism which deforms PVDF chains and PMMA chains exactly in the same way at all deformations, a complete compensation of birefringence for all stages of
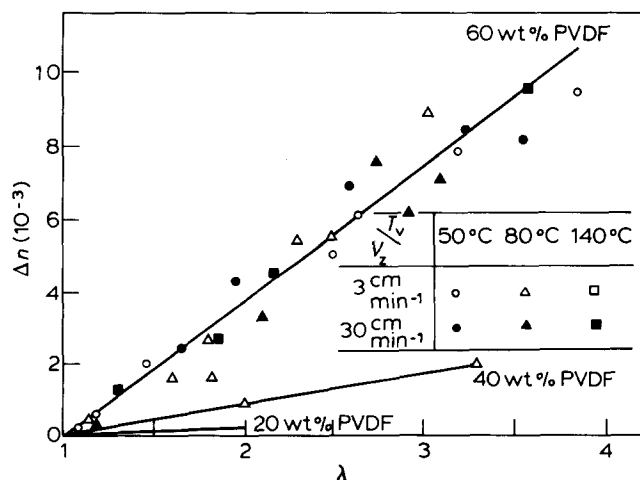


**Figure 2** Birefringence $\Delta n$ vs. draw ratio $\lambda$ of three amorphous PVDF/PMMA blends having different compositions, stretched at 50, 80 or 140°C with a draw speed of either 3 or 30 cm min$^{-1}$
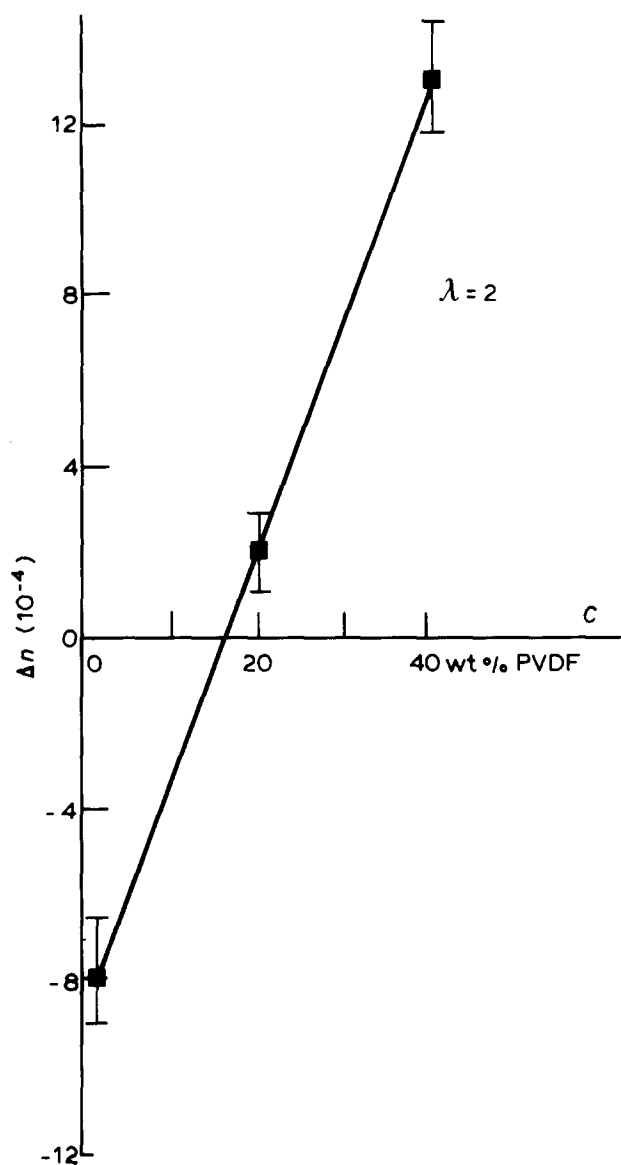
**Figure 3** Determination of the composition of zero birefringence: Birefringence vs. composition of amorphous PVDF/PMMA blends stretched to a draw ratio of 2 at equivalent conditions during drawing (see text for details). Note the zero-crossing, which gives the composition of zero birefringence

deformation would exist for a blend of PVDF and PMMA with an appropriate composition. Such a compound would ideally be free of birefringence, no matter what processing conditions and resulting molecular orientation would be present. Therefore it would be an attractive material for optical applications. In order to determine how close PVDF/PMMA blends of suitable compositions come to this idealized case, PVDF/PMMA blends of compositions have been prepared, which were closely spaced around the composition 17/83 where zero-crossing of birefringence occurs, as determined from *Figure 3*. The blends were prepared in the compositions 20/80, 18/82, 16/84, 14/86 and 00/100 (PVDF/PMMA) for comparison. Sheets of 2 mm thickness were prepared in a hot press and dog-bone shaped samples of 70 mm length were cut from those sheets[4]. Then, the samples were uniaxially stretched at 10 mm min$^{-1}$, up to different draw ratios in a heat chamber at 'equivalent draw temperatures' $T_d^*$. This 'equivalent draw temperature' was chosen for each blend composition individually to have the same temperature difference to the glass transition temperature

of that individual blend. This was done to ensure that every composition experienced equivalent draw conditions, in order to allow meaningful comparisons. In the composition range considered here, the glass transition temperature $T_g^B$ of the blends changes almost linearly with composition. The values taken for $T_g^B$ are shown in *Table 1*.

*Figure 4* shows the birefringence of the four different, closely spaced PVDF/PMMA blends in comparison with that of pure PMMA, after they have been stretched to the same draw ratio of 2 at different equivalent draw temperatures $T_d^*$. One half of those samples was annealed after stretching for 1 h at 25°C below their individual glass transition temperatures. This was done in order to release internal stress, causing stress birefringence, which results from deformation of molecular bonds. One other possible contribution to birefringence is form birefringence. But form birefringence occurs only in optically inhomogeneous materials[1], and therefore is not considered here.

*Figure 4* shows that a blend of composition 18/82 exhibits extremely low levels of birefringence. The values are about 50 times smaller than for pure PMMA. Additionally, this effect does only weakly depend upon the draw temperature. This blend therefore does not require carefully controlled processing temperatures during drawing.

*Figure 5* shows that an ideally compensated behaviour does not exist here, specifically at higher draw ratios. The
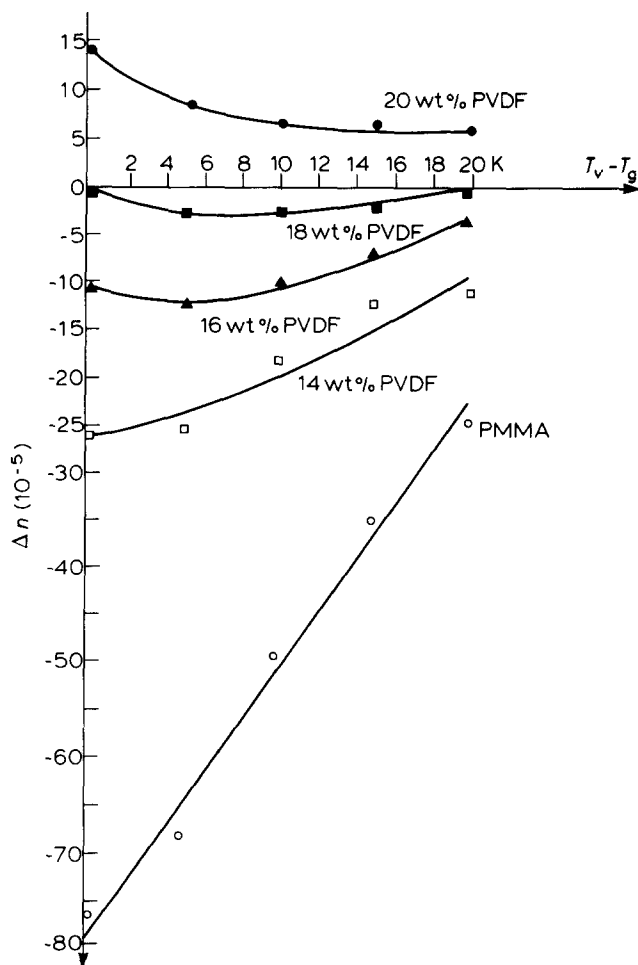


**Figure 4** Birefringence of PVDF/PMMA blends after stretching to a draw ratio of 2 at different temperatures above their glass temperature $T_g^B$ ($v = 10$ mm min$^{-1}$). The blends have compositions closely spaced around the point of zero crossing (in *Figure 3*)

birefringence compensation effect becomes significantly smaller if the draw ratio becomes larger than 2. For draw ratios up to about 2, an almost complete cancellation of birefringence is achieved, however, for a blend, having the composition 18/82—regardless of the processing conditions. For draw ratios larger than 2, it is still possible to get a fairly good compensation if the draw ratio and the blend composition are chosen appropriately. For instance, for a draw ratio of 2.8 one obtains zero birefringence by using a PVDF/PMMA blend having the composition 20/80.

The conclusion is that an almost complete compensation of birefringence is obtained, by using a blend with the composition 18/82, if the draw ratio is smaller than about 2. For draw ratios between 2 and 3, the blend composition and draw ratio have to be chosen in dependence upon each other, in order to get complete compensation of birefringence. Draw ratios larger than 3 usually are difficult to realize because of sample failure, and are therefore not as relevant in a technological sense. Scientifically of interest is the reason for the deviation of the actual behaviour from an idealized behaviour. Birefringence measurements as described here and elsewhere might be useful as a sensitive tool for studying the deformation behaviour of different polymer components in a blend[13] or a copolymer.

## General considerations

Experimental data is presented above on a polymer blend system where one component (PMMA) has

**Table 1** Glass transition temperature $T_g^B$ of closely spaced PVDF/PMMA blends. These values have been taken from the determination of an equivalent draw temperature $T_g^*$, and adjusting the draw temperature for each blend to the same temperature difference relative to its individual glass temperature

| Composition, wt% PMMA | $T_g^*$ (°C) |
|---|---|
| 100 | 108 |
| 86 | 87 |
| 84 | 84 |
| 82 | 81 |
| 80 | 78 |

interesting optical properties. These good optical properties can obviously be improved even more by blending it with smaller amounts of PVDF, without sacrificing other essential properties. However, this procedure requires compatibility between both polymers. In the case of polymers, the compatibility between two kinds of polymers is the exception rather than the rule. Therefore the blending concept applied here cannot easily be transferred to other optical polymers, such as poly-(carbonate) or poly(styrene), where optical birefringence is a much more serious problem than in the case for PMMA. Polycarbonate (PC) and polystyrene (PS) display much larger values of birefringence than PMMA[12]. Therefore a blending partner is needed with much higher birefringence values of the opposite sign, in order to be able to compensate birefringence sufficiently, in particular at low concentrations only. This polymer has to be compatible with PC or PS. Such a polymer will be difficult to find.

Relief from the compatibility-constraint is gained, if one considers statistical or block copolymers. Here a much larger number of polymers can be combined with each other, in order to obtain the right combination, which gives a resin that can be processed and does not show optical birefringence. Also, the dependence of the compensation effect at large draw ratios on the deformation as discussed might be eliminated.

Finally, graft copolymers which reduce birefringence effects are feasible.
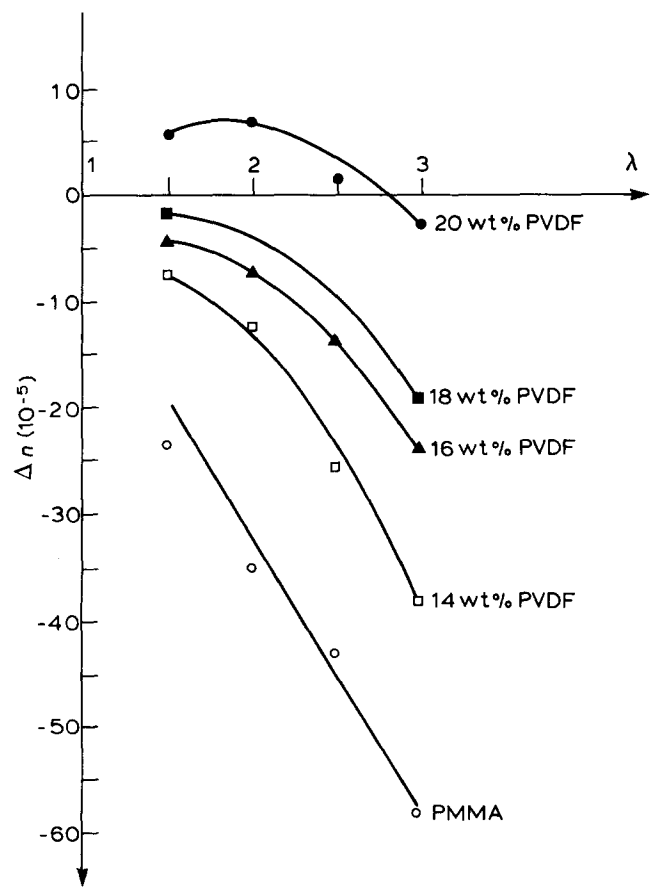
## ACKNOWLEDGEMENTS

**Figure 5** Birefringence of closely spaced PVDF/PMMA blends in dependence of the draw ratio. The samples have been stretched 15°C above their individual glass temperature (see *Table 1*) with a draw speed $v$ of 10 mm min$^{-1}$

## REFERENCES

1    Ward, I. M. 'Structure and Properties of Oriented Polymers', J. Wiley and Sons, 1975
2    Marchant, A. B. *Proc. SPIE*, Vol. 421 1983, p. 43
3    Prest, W. M. US Pat. 4 373 065 (Feb. 8, 1983)
4    Borngräber, B. Studienarbeit, TH Darmstadt, 1983
5    Paul, D. R. and Altamirano, J. O. *Adv. Chem. Ser.* 1975, **142**, 371
6    Nishi, T. and Wang, T. T. *Macromolecules* 1985, **8**, 909
7    Hahn, B. R. *PhD Thesis*, Deutsches Kunststoff-Institut, Darmstadt, FRG, 1983
8    Hahn, B. R., Wendorff, J. H. and Yoon, D. Y. *Macromolecules* 1985, **18**, 718
9    Schmidt, J. M. US Patent 3 459 834 (Aug. 5, 1969)
10   van Krevelen, D. W. 'Properties of Polymers', Elsevier, Amsterdam, 1972
11   Wendorff, J. H. *J. Polym. Sci. Polym. Lett. Edn.* 1980, **18**, 445
12   Hennig, J. *Colloid Polym. Sci.* 1981, **259**, 80