Changes of Dichroism in Polypropylene Films

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Polypropylene films used in tubular power capacitors were studied. IR spectroscopy was used to obtain information about their physicochemical properties. Reliable data on the supramolecular structure were obtained from measurements of polarized IR spectra and dichroism calculated from them. The changes of dichroism as a consequence of dipping the films in liquid dielectric at elevated temperatures are discussed.

Systems made from polypropylene chains do not have the polymer chains explicitly oriented in space. The arrangement of chains or segments of macromolecules varies from amorphous to highly spatially oriented [1—3]. The spatial or even planar rearrangement of polypropylene chains occurs during one- or two-directional deformations of polymer material, as a consequence of axial tension. For polypropylene (PP) films, anisotropy is a direct result of their production. As PP films are used in electrical industry as solid dielectrics for power capacitors, it is very important to know their properties. Therefore, we investigated biaxially oriented polypropylene films (BPP). The machine direction is supposed to be identical with 0° on the scale of the polarizer.

The orientation of macromolecules was measured as dichroism *D*, calculated from polarized IR spectra [1, 4]. Changes of dichroism in BPP films (as direct structural changes) were evaluated during the interaction of the films with liquid dielectrics. Dipping of BPP films in liquid was performed at 90 °C.

EXPERIMENTAL

Commercial BPP films produced in Slovakia (Tatrasvit, Svit) „Tatrafan I" and „Tatrafan II" were studied. Results were compared with those obtained from the French BPP film „Safidiep" (thickness 12 μm ± 3 %). The thicknesses of „Tatrafan I" and „Tatrafan II" films were 12 μm and 25 μm ± 3 %, respectively. Dielectric liquid „Suresol" (pure isopropylbiphenyl) was used as well as the compound „PAB" (a mixture of isopropylbiphenyl (≈ 80 mass %) and low-molecular hydrocarbons).

IR spectra were recorded using a two-beam spectrometer Specord M-80 with a built-in polarizer (polyethylene film with grid, $k = 1200$ lines/mm). The measurements were taken in the $\tilde{\nu}$ range 800—1200 $\mathrm{cm^{-1}}$ [4]. Four marked absorption bands were evaluated. IR dichroism was calculated from these bands (Fig. 1) [4, 5]

$\tilde{\nu} = 1168\ \mathrm{cm^{-1}}$: deformation vibrations of CH_3 and CH_2 in crystalline regions (typical for BPP)
$\tilde{\nu} = 998\ \mathrm{cm^{-1}}$: skeletal vibrations of C (typical for isotactic polypropylene)
$\tilde{\nu} = 974\ \mathrm{cm^{-1}}$: deformation vibrations of CH_3, CH_2, and CH arranged perpendicularly to the main chain orientation
$\tilde{\nu} = 841\ \mathrm{cm^{-1}}$: twisting oscillations of CH_3, CH_2, and CH (typical for isotactic PP).

The measurements were taken with the polarizer oriented either parallelly (=) or perpendicularly (⊥) to the machine direction. Dichroism was calculated from the absorbance values using the formula

$$D = \frac{A\,=}{A\,\perp} \tag{1}$$

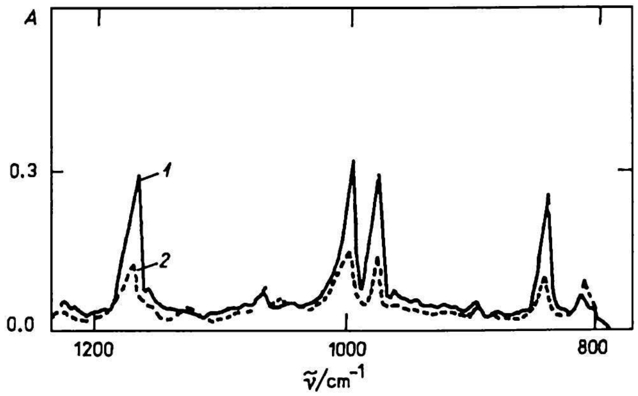

Fig. 1. IR spectrum of polypropylene film (Tatrafan I, 12 μm) studied under two different possible positions of the polarizer. ——— Polarizer makes 0° angle with the axis of PP film; – – – – polarizer makes 90° angle with the axis of PP film. *1.* *A* = ; *2.* *A*⊥ .

For measurement of the PP films, the axis of machine direction was conventionally made identical with the main axis of the polymer.

The BPP films were exposed to liquids at (90 ± 1) °C for 1 h, 2 h, 5 h, 15 h and 24 h, respectively.

The measurements were performed in one fixed position of the sample to minimize errors resulting from differences in thickness caused by inhomogeneity of films. The orientation factor f was calculated from the absorption band at $\tilde{\nu}$ = 974 cm^{-1}

$$f = \frac{D(974) - 1}{D(974) + 2} \qquad (2)$$

RESULTS AND DISCUSSION

Biaxially oriented isotactic polypropylene films (BPP) with a high degree of orientation were studied. In such systems, the values of dichroism greatly differ from 1 ($D > 1$ is conventionally denoted as π dichroism and $D < 1$ as σ dichroism). It was shown that the dichroism values of the measured samples calculated from the corresponding absorption bands changed as a result of interaction between BPP films and liquid dielectrics [6]. The effect of the duration of interaction between the liquids and the polypropylene films was also studied. This process of interaction we called „thermochemical stress“ of the films. In the literature we have not found any work dealing with the influence of „thermochemical stress“ of PP films on D.

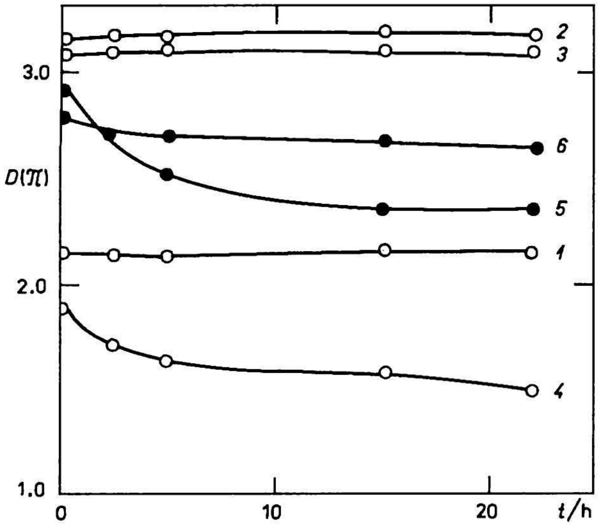

Fig. 2. Dependence of the dichroic ratio D (π) on time of „thermochemical stress“ of the Safidiep sample. Lines *1* and *4* D are derived from the absorption bands at $\tilde{\nu}$ = 1168 cm^{-1}, *2* and *5* D from the absorption bands at $\tilde{\nu}$ = 998 cm^{-1}, *3* and *6* D from those at $\tilde{\nu}$ = 841 cm^{-1}. ○ In Suresol; ● in PAB.

The influence of both liquid dielectrics (Suresol, PAB) on all three types of BPP (Safidiep, Tatrafan I, Tatrafan II) was studied. The intensities of absorption bands at 841 cm^{-1}, 998 cm^{-1}, and 1168 cm^{-1} were also measured and corresponding values $D(841)$, $D(998)$, $D(1168)$ (Fig. 2, lines *1—3*) were calculated. IR spectra of BPP Safidiep „thermochemically stressed“ in Suresol liquid have shown that values from absorption bands, as well as dichroism values calculated from them, do not significantly change.

Similar procedures were followed for Safidiep in PAB liquid. A significant decrease of dichroism was observed during the first two hours (Fig. 2, lines *4—6*). Maximal changes were also found during the first two hours. Further dipping (up to 24 h) caused no further significant changes.

Tatrafan I and Tatrafan II were similarly „thermochemically stressed“ in both liquids. For Tatrafan I, when dipping it in Suresol liquid, no significant changes of D were observed, *i.e.* similar to the previous results (Fig. 3, lines *1—3*). It is surprising that dipping this sample in PAB liquid had the opposite effect manifested in Safidiep sample; the values of dichroism in this case increased (Fig. 3, lines *4—6*).

Similar results were also obtained with the Tatrafan II film. No changes of D were observed upon dipping BPP film in Suresol liquid (Fig. 4, lines *1—3*). On dipping the sample in PAB, the D values increased but not to the same extent as for Tatrafan I (Fig. 4, lines *4—6*).

From the gained results it is evident that in all the three types of films the „thermochemical stress“ by liquid Suresol causes only minor changes of dichroism values (Figs. 2—4). Probably no such interactions between the polymer chains and the liquid dielectric occur which cause structural changes or rearrangement of chains [4]. PAB liquid caused significant changes of dichroism in all samples. While

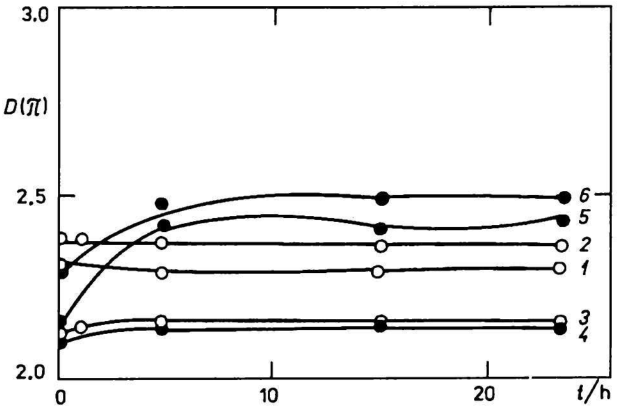

Fig. 3. Dependence of the dichroic ratio D (π) on time of „thermochemical stress“ of the Tatrafan I sample. Denotation of the lines is the same as in Fig. 2.

Table 1. Values of the Dichroic Ratio *D* and of the Orientation Factor *f* for the Samples without Dipping and with Dipping (24 h in Suresol and PAB)

No.	Sample	Thickness	*D* without dipping		*D* with dipping 24 h		*f* without dipping		*f* with dipping 24 h	
		μm	SUR	PAB	SUR	PAB	SUR	PAB	SUR	PAB
1	Safidiep	12	2.10	1.85	2.10	1.70	0.268	0.220	0.268	0.189
2	Tatrafan I	12	2.05	2.00	2.05	2.25	0.259	0.250	0.259	0.294
3	Tatrafan II	25	1.95	1.98	1.92	2.15	0.240	0.246	0.235	0.277

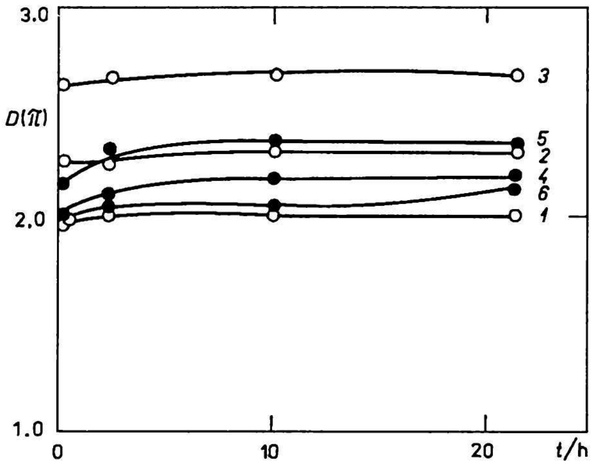

Fig. 4. Dependence of the dichroic ratio *D* (*π*) on time of „thermochemical stress" of the Tatrafan II sample. Denotation of the lines is the same as in Fig. 2.

in the case of Safidiep film (Fig. 2) a decrease of dichroism, calculated from all absorption bands, was observed, both Tatrafan I and Tatrafan II are showing an increase of *D* (Figs. 3 and 4).

The values of orientation factor *f* (calculated from eqn (2) by evaluating the absorption band at $\tilde{\nu}$ = 974 cm^{-1}) for Safidiep decreased approximately by 4 %. In Tatrafan I and Tatrafan II the value increased by about 4 % and 2 %, respectively. Results are given in Table 1.

In the case of Safidiep foil, the results can be explained as penetration of low-molecular fraction PAB during „thermochemical stressing" between crystalline fractions of polymer chains. This disturbance of polymer chains causes reduction of the crystalline fraction in BPP films (decrease in *D* and *f*). Contrary to these results in the case of the BPP films Tatrafan I and Tatrafan II this effect is probably overlapped by another effect due to which low stability mesomeric organization of supramolecular systems is gradually changing to a more stable crystalline form [7]. These facts probably are very closely related to the technological procedure of BPP films preparation.

Less significant changes of the dichroism of Tatrafan II foils, as compared to Tatrafan I, can probably be explained by different thickness of these films (12 μm and 25 μm, respectively). In the case of only „thermostress" on PP foils, no significant changes were observed in the dichroic ratio *D*.

The dielectric parameters of foils (ε_r and tg δ) are not changed after dipping in the dielectric liquids.

CONCLUSION

In this paper a possible evaluation of physical properties of polypropylene films, used in electrical industry as solid dielectrics in power capacitors, is proposed. The films were exposed to a prolonged exposure to two different liquid dielectrics at 90 °C. It was demonstrated that dipping the samples in Suresol liquid did not lead to significant changes of *D* and *f* parameters. However, different behaviour was observed upon dipping the samples in PAB liquid. A decrease of the dichroic ratio was observed in Safidiep sample, whereas an increase of the dichroic ratio, and the orientation factor *f*, was observed in Tatrafan I and Tatrafan II foils.

REFERENCES

1. Ward, J. M., in *Structure and Properties of Oriented Polymers.* (Ward, J. M., Editor.) P.150. Applied Science Publishers, London, 1975.
2. Iwato, N., Tanaka, H., and Okajama, S., *J. Appl. Pol. Sci. 19*, 303 (1975).
3. Abe, K. and Yanagisawa, K., *J. Polym. Sci. 36*, 536 (1959).
4. Jambrich, M., *Štruktúra a vlastnosti vlákien* (Structure and Properties of Fibres). Slovak Technical University, Bratislava, 1987.
5. Miglierini, K., Adamčík, V., and Polakovič, J., *Chem. Prům. 40/65* (11—12), 570 (1990).
6. Sandeman, J. and Keller, A., *J. Polym. Sci. 19*, 401 (1956).
7. Diačik, J. and Jambrich, M., *Chem. Zvesti 14*, 540 (1960).

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